ADSORPTION OF COPPER AND NICKEL ON NATURAL SAUDI ARABIAN CLAY AND BENTONITE

BY

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For my family

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LIST OF ABBREVIATIONS

BET : Brunauer- Emmet-Teller.

$C_{adsorbed}$: Concentration of metals that were adsorbed into the adsorbent (mg/L).

C_e : Equilibrium concentration (mg/L).

C_0 : Initial concentration of solution (mg/L).

$C_{remaining}$: concentration of metals that remaining in solution after removing adsorbent (filtering) mg/L

EDX : Energy-dispersive X-ray spectroscopy.

K_1 : Pseudo first order adsorption rate coefficient ($1/min$).

K_2 : Pseudo second order adsorption rate coefficient ($g/(mg* min)$).

K_f : Freundlich coefficient measure the capacity of the adsorbent.

K_L : Langmuir constant measure the affinity of adsorbate for adsorbent (L/mg).

M : Mass of adsorbent (g).

MCL : The maximum contaminant level (mg/L).

n_f : Freundlich constant for measuring parameter of how affinity for the adsorbate changes with changes in density of adsorption.

q_e : Adsorption capacity at equilibrium (mg/g).

q_{max} : Maximum adsorption capacity (mg/g).

q_t : Adsorption capacity at any time (mg/g).

R_L : Dimensionless equilibrium parameter for Langmuir isotherm.

SEM : Scanning electron microscopy.

V : Volume of solution (L).

XRD : X-ray diffraction.

XRF : X-ray fluorescence.

ABSTRACT

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Thesis Title : Adsorption of Copper and Nickel on Saudi Arabian Clay and Bentonite

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In this work, Saudi Arabian bentonite, clay and the combinations of bentonite-clay have been investigated as adsorbents to remove copper and nickel from aqueous solution. The effects of contact time (5-480 min), the ratio of bentonite to clay, initial adsorbate concentration (20-100 mg/L), adsorbent dosage (0.2-1 g), and pH (3.5-8) were investigated and optimum conditions were experimentally determined. The clay material and bentonite were obtained from various sites in the Eastern Province of Saudi Arabia and were thoroughly characterized using SEM, BET, CEC, XRF and XRD techniques. The results show that Saudi Arabian clay and bentonite can be considered as adsorbents for removal of copper and nickel from wastewater. Also, it observed that the ratio of bentonite to clay had a significant impact on the adsorption capacity where an increase in this ratio results in a decrease the adsorption capacity of copper. However, the results show that an increase in this ratio results in an increase the adsorption capacity of nickel. The adsorption capacity (q_e) of copper and nickel was very fast in the first few minutes and then decreased until attainment of the equilibrium. The equilibrium was reached at 30 min and 45 min for Cu and Ni with adsorption capacities of 8.7 mg/g and 8.9 mg/g respectively using bentonite alone. However for clay alone, the equilibrium was reached at 240 min and 360 min for Cu

and Ni with adsorption capacities of 16 mg/g and 7.7 mg/g respectively. In addition, the results show that the removal efficiency decreased with an increasing in the initial metal ion concentration of Cu and Ni. While an increase in the amount of adsorbent and/or pH the removal efficiency increased. On the other hand, the adsorption capacities for copper and nickel increased with the increase in pH and/or initial metal ion concentrations, however as the amount of adsorbent increased the adsorption capacities decreased for all combination adsorbents. Additionally, this study investigated the adsorption kinetics, and isotherms of copper and nickel. The results show that the experimental data had a good agreement with pseudo-second-order model with R^2 of 0.96 to 1. Furthermore, the results show that Cu and Ni removal had a good fitting with both Langmuir and Freundlich isotherm models for all combinations of clay and bentonite adsorbent with R^2 of 0.91 to 0.99.

ملخص الرسالة

الاسم الكامل: خالد سعيد منيف

عنوان الرسالة: إزالة النحاس والنيكل باستخدام تقنية الامتزاز بواسطة الطين و البنتونيت السعودي

التخصص: هندسة مدنية

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في هذا البحث الطين وخليط الطين مع البنتونيت والبنتونيت استخدمت كماده ممتصة لإزالة النحاس والنيكل من السوائل. كذلك تم دراسة تأثير كلا من مدة الاهتزاز (0-480 دقيقة)، و نسبة البنتونيت الى الطين، و كمية المادة الممتصة (0.2 – 1 جم)، و التركيز الاولي للمعدن في السائل (20-100 مجم لكل لتر)، و درجة حموضة السائل (3.5-8). الطين المستخدم في هذا البحث تم الحصول عليه من المنطقة الشرقية السعودية والبنتونيت تم تزويده عن طريق شركة الرياض للإساسات. تم عمل تحليل للطين والبنتونيت باستخدام تقنيات مختلفة. النتائج الحاصل عليها من هذا البحث اظهرت ان الطين و البنتونيت يعتبر مادة جيدة لازالة النحاس و النيكل من المياة الملوثة. ايضا وجد ان نسبة الازالة تزيد مع زيادة نسبة البنتونيت الى الطين بالنسبة للنيكل. لكن العكس مع النحاس حيث ان نسبة الازالة تنقص كلما زادت نسبة البنتونيت الى الطين. اضافة الى ذلك الامتصاص لكلا من النحاس والنكيل كان سريعا في الدقائق الاولى ومن ثم يتناقص قليلا حتى الوصول الى حالة التشبع (الاتزان). حيث ان وقت التشبع (الاتزان) للنحاس كان عند الدقيقة 30 مع كمية امتصاص 8.7 مجم/ جرام والنيكل كان عند الدقيقة 45 مع كمية امتصاص 8.9 مجم/جرام باستخدام البنتونيت. اما بالنسبة للطين كان الاتزان بعد مرور 240 دقيقة مع كمية امتصاص 16 مجم/جرام للنحاس و بعد مرور 360 دقيقة مع كمية امتصاص 7.7 مجم/جرام. كذلك وجد ان نسبة الازالة مع النحاس والنيكل تتناسب طرديا مع كلا من كمية المادة الممتصة و درجة حموضة السائل و عكسيا مع التركيز الاولي للمعدن في السائل. كذلك وجد ان الكمية الممتصة للنحاس و النيكل تتناسب طرديا مع كلا من درجة حموضة السائل و التركيز الاولي للمعدن في السائل و عكسيا مع كمية المادة الممتصة. بإلاضافة الى ذلك تم كلا من الداسة الحركية و الأيسوثرم و النتائج اظهرت ان البيانات لكل من النحاس والنيكل تتطابق مع نموذج الدرجة الثانية بالنسبة للدراسة الحركية و مع كلا من نموذج انجميور ونموذج فروندليتش بالنسبة للدراسة الأيسوثرم مع معامل تصحيح 0.91-0.99.

[CHAPTER 1]

INTRODUCTION

Recently, Saudi Arabia and elsewhere have been witnessing a massive development in industries especially petrochemical industries. Currently, the Kingdom has large number of oil refinery plants with huge number of petrochemical and other manufacturing plants. Therefore, these industries release large number of different pollutants such as heavy metals into the surrounding environment. These pollutants (i.e. heavy metals) which are classified as toxic substances may enter the environment (e.g. aquatic compartments, and groundwater) through a different routes, as a result, they are potential hazards to the environment and human health [1,2].

Heavy metals pollutions are considered as one of the most important environmental challenges. As consequence, a number of physical-chemical technologies such as ion exchange, chemical precipitation, membrane filtration, adsorption, solvent extraction, electrochemical, etc. have been used and developed for removal of heavy metals. However, each technology has its limitations with some relatively more expensive[3,4]. Among the existing technologies, adsorption becomes an effective and economic technique in treatment wastewater contaminated by heavy metals.

Adsorption technology use various adsorbents such as activated carbon, sand, eggshell, zeolites, olive stones, clay, wood sawdust … etc. However, available commercial adsorbents (e.g. activated carbon) are very expensive, while natural and locally available adsorbent such as clay and bentonite are cheap. Consequently, numerous researches have made significant efforts in developing and improving the effectiveness of adsorption, which make it more competitive in terms of performance and cost. These trends include modified activated adsorbents to increase the surface area and the performance.

1.1 Problem Statement

In this thesis, mixtures of bentonite and clay in different ratios as available local materials are prepared and characterized to use as adsorbents. These adsorbents are used to remove copper and nickel from aqueous solution under different operating parameters with the hope of achieving an efficient removal. If proven efficient, this mixture will be seen to be an effective alternative to the widely used activated carbon in treatment wastewater contaminated by heavy metals.

1.2 Aims and Objectives

In this study, the main objective is to investigate heavy metals removal from synthetic wastewater using different mixtures of natural clay-bentonite obtained from Saudi Arabia. To achieve the objective of this work, two heavy metals (copper (Cu), and nickel (Ni))

were considered for removal from the simulated contaminated wastewater using five different mixtures ratios of clay-bentonite. These mixtures ratios are 100% clay, 90% clay with10% bentonite, 70% clay with30% bentonite, 50% clay with 50% bentonite, and 100% bentonite. Also, this work aims to investigate optimum operation conditions namely; shaking time, mass of adsorbent, pH, and initial metal concentration.

The specific objectives of this work are:

a) Study the adsorption behavior of copper and nickel ions in single component onto bentonite, the combinations of bentonite-clay, and clay alone under different operation parameters.
b) Characterize the adsorbents (i.e. clay and bentonite) using XRD, CEC, XRF, BET, SEM, and EDX.
c) Investigate the adsorption equilibrium and the maximum adsorption capacity of Cu and Ni ions onto adsorbents.
d) Examine the effect of the shaking time, pH, initial adsorbate concentration, and the mass of adsorbent on the removal of metals.
e) Investigate the kinetic study and the best fitted models for adsorption process.
f) Determine the best fitted adsorption isotherm model at the equilibrium.
g) Determine the optimum mixing ratio of clay- bentonite for removal of Cu and Ni ions from wastewater.

1.3 Organization of Thesis

This thesis has been subdivided into five chapters. Definition of the problem, the work objectives, organization, and contribution of this research are introduced in chapter one. Chapter 2 has been present relevant literature review. The methodology, detail experimental, analysis techniques, and different mathematical modeling are detailed in chapter 3. The physical-chemical characterization of adsorbents, the outcomes of the data, analysis data, models, and the effect of various parameters on adsorption are discussed on chapter 4. Finally in chapter 5, over all summery, conclusions, and recommendation for further work are presented.

[CHAPTER 2]

LITERATURE REVIEW

Due to the increase in generating large number of different pollutants such as heavy metals into the surrounding environment from industries and other sources, treatment of wastewater using various technologies such as adsorption become an urgent and top priority to researchers, environmentalist and regulatory governments. Two of heavy metals of major environmental concern today are copper (Cu), and nickel (Ni). To remove these metals there are many available technologies such as chemical precipitation, membrane filtration, reverse osmosis, adsorption, solvent extraction, ion exchange, electrochemical, etc., but some of these technologies have limitations and are proportionally expensive[3,4].

2.1 Heavy Metals and Their Environmental Impacts

Due to toxicity of metals, they are considered as one of the most significant pollutants in the environment, especially for agriculture, food safety, animals, and human health[3]. ‘‘ The term heavy metals refers to any metallic element that has a relatively high density and is toxic or poisonous even at low concentration ” [5]. ‘‘ Heavy metals is a general collective term, which applies to the group of metals and metalloids with specific gravity greater than 5.0 or 5 times more than water and with atomic weights between 63.5 and 200.6 ”, examples of heavy metals include Copper (Cu), and Nickel (Ni)[6]. Heavy metals are naturally created in the Earth's crust, and they cannot be degraded or destroyed.

They can enter human bodies through drinking water, air, and food. Drinking water can be contaminated by heavy metals via discharged wastewater from different sources such as industries[5]. Also, the presence of metals in the soil is a major concern due to their accumulation in the plants causing serious problems to the human and environment, including environmental pollution, diseases, and maybe lead to death if they exceed standard limits[7]. According to the World Health Organization (WHO)[8], various heavy metals (e.g. Arsenic (As), Cadmium (Cd), Chromium (Cr (VI)), Copper (Cu), Lead (Pb), Nickel (Ni), etc. are considered as the most toxic contaminants.

2.1.1 Copper and Its Effect on the Environment

Copper is a chemical element with two natural isotopes (^{63}Cu, and ^{65}Cu), atomic number 29, and atomic weight 63.55. It is melt at 1083 °C, and boil at 2595 °C. Cu has density of 8.9 g.cm^{-3} at 20°C, Vander Waals radius of 0.128 nm, and a blue color in solution, and occurs in I , and II oxidation states[9,10]. Also, copper is one of the important ingredients to human life in small concentrations, however it is considered as one of the toxic metals. In other words, it is considered as both an essential nutrient and a drinking-water pollutant which can cause health hazard and diseases such as Wilson's disease, intestinal irritation, stomach, vomiting, cramps, convulsions, anemia, liver and kidney damage, or even death[3,811,12]. As a result, the wastewater which exceed the standard limit of copper should be reduced to prevent accumulation in the surrounding environment. Table 1 summarizes the maximum contaminant level (MCL) values for copper in drinking water according to different organizations.

Table 1: The maximum contaminant level (MCL) values for Copper in drinking water.

Organization	MCL (mg/L)	Ref.
World Health Organization (WHO)	2	[8] [13]
United States Environment Protection Agency (U.S. EPA)	1.3 0.25	[13,14,15] [16,17]
Saudi Arabian Standards Organization (SASO)	1.0	[18]

Table 2: The maximum contaminant level (MCL) values for Nickel in drinking water.

Organization	MCL (mg/L)	Ref.
World Health Organization (WHO)	0.07	[8]
United States Environment Protection Agency (U.S. EPA)	0.2	[16,17]

2.1.2 Nickel and Its Effect on the Environment

Nickel is a metallic element with atomic number of 28, and atomic mass of 58.71. It exists in oxidation states 0 and II; under certain conditions I and III oxidation states can occur, but are not stable in aqueous solutions. Ni is colorless in solution, and has density of 8.9 $g.cm^{-3}$ at 20°C, and Vander Waals radius of 0.124 nm[9,19].

In addition, nickel is a nutritionally essential substance for human body in small amounts to produce red blood cells but, in excessive levels may cause health problems such as heart and liver damage, reduced body weight, skin dermatitis[5], pulmonary fibrosis[3], allergies, infertility, renal and hepatic disturbances, gingivitis, migraines, stomachache, insomnia, and nauseas[20]. Therefore, the wastewater that contaminated with high levels of nickel should be treated to prevent health, and environmental problems. Table 2 summarizes the maximum contaminant level (MCL) values for nickel in drinking water according to different organizations.

2.2 Technologies Used for Heavy Metals Removal from Wastewater

In recent years, a wide variety of treatment methods have been studied for heavy metal ions removal from wastewater include chemical precipitation, reverse osmosis, flotation, electrochemical, membrane filtration, and adsorption as reviewed by Fenglian et al.(2011), and Barakat (2011).

2.3 Adsorption Technology

One of the most common treatment technique for removal of metals from wastewater is adsorption which considered as an effective, economic, and simple method[21].

2.3.1 Fundamentals of Adsorption

Process of transfer a substance from the solution or liquid phase (the adsorbate) to the adsorbent (solid phase) i.e. ions from water to the soil is called adsorption[22]. Basically, adsorption is mass movement process by which the molecules or ions present in one phase tend to concentrate or accumulate on the surface of another phase, and this process is divided to three types; chemical, physical and exchange adsorption [23]. The mass (i.e. ions) which is removed from liquid phase is called adsorbate, and the gas, liquid, or solid phased that the adsorbate accumulates on its surface is called adsorbent[24]. Also, the adsorption capacity is the amount of heavy metal uptake (adsorbate) per unit mass of solid (adsorbent). The case of liquid-solid interface is taken in consideration because it is related to this work.

The investigate of kinetics gives a concept about the mechanism of the adsorption reactions as well as the reaction pathways where, the kinetics describe the residence time of adsorbate remove onto the adsorbent surface that estimate the solute uptake [25]. Gupta & Bhattacharyya,2011[26] reported that the adsorption process (kinetics) carried out in three steps and the slowest step determine the kinetics of the adsorption. These steps are; (i) movement of the ions to the external surface of the adsorbent in the solution through the bulk, (ii) transport of the pollutant through the liquid film attached to the adsorbent surface, and (iii) interactions of adsorbate with the surface atoms of the adsorbent resulting chemisorption. Several adsorption system used to describe the kinetics adsorption process, the most widely used are the pseudo-first-order (Lagergren), pseudo-second-order.

2.3.1.1 Pseudo First Order

The earliest known equation describe the rate of adsorption in the liquid phase is that presented by Lagergren (pseudo first order equation)[26]. According to Plazinski et al[27] the differential form of this equation can be expressed in the following formulation (1), and by integrate equation (1) to the boundary conditions of $at\ t = 0\ \rightarrow\ q_t = 0\ and\ t = t\ \rightarrow q_t = q_t$ getting equation (2). The value of k_1 and q_e can be determined from the slope that getting by plotting($Ln(q_e - q_t)\ VS.\ t$).

$$\frac{dq(t)}{dt} = k_1\ (q_e - q_t) \qquad (1)$$

$$\ln(\ q_e - q_t) = -k_1\ \mathrm{t}\ +\ \ln(q_e) \qquad (2)$$

2.3.1.2 Pseudo Second Order

The pseudo second order kinetics assume that the controlling step is the chemical reaction including valance force with respect to the exchange ions[28]. According to Gupta & Bhattacharyya[26], the most widely used form of the pseudo second order is as can be expressed as in equation (3). Also by integrate equation (3) to the boundary conditions of $at\ t = 0 \rightarrow q_t = 0\ and\ t = t \rightarrow q_t = q_t$ getting equation (4). The value of k_2 and qe can be determined from the slope that getting by plotting($t/q_e\ VS.\ t$).

$$\frac{dq(t)}{dt} = k_2 * (q_e - q_t)^2 \qquad (3)$$

$$\frac{t}{q_t} = \frac{1}{k_2 * q_e^2} + \frac{t}{q_e} \qquad (4)$$

Several researchers studied the kinetics adsorption for different type of minerals to remove copper and nickel. Gupta & Bhattacharyya[26] and Malamis & Katsou[28] reported that the adsorption of on different clays fitted to the pseudo second order model and this model gives a close prediction for the equilibrium adsorption capacity. On the contrary, the pseudo-first-order model could not provide reasonable equilibrium adsorption capacity, even though it has high correlation with the experimental data.

In adsorption science, the fundamental concept is that named as the adsorption isotherm. At given temperature and at equilibrium, the relationship between the metal concentration in solution and adsorption capacity (qe) is called adsorption isotherms[23,29]. In other word, " sorption isotherm is the equation or curve that connects the metal concentration that has been adsorbed on the solid phase with metal concentration in the solution at equilibrium for specific temperature "[28]. Several isotherm equations used to describe adsorption isotherms, the most widely used are Langmuir, and Freundlich isotherms.

2.3.1.3 Langmuir Isotherm

Langmuir isotherm which is an empirical equation and it is considered as one of the most widely used isotherms for the explanation of adsorption equilibrium. This equation is derived from kinetic studies and assumes that adsorption is limited to monolayer (i.e. only one adsorbate can be adsorbed to a single site on the adsorbent surface). Also, the affinity for the adsorbate on a given site of the adsorbent is equal[23,29,30]. Febrianto et al.[29], and based on these assumptions, and kinetic principles the Langmuir equation can be written in the following form (5), and to determine the coefficients $\mathbf{q_{max}}$ and $\mathbf{K_L}$ equation (5) is linearized as in equation (6).

$$q_e = q_{max} \frac{K_L C_e}{1 + K_L C_e} \qquad (5)$$

$$\frac{1}{q_e} = \frac{1}{q_{max} K_L}\left(\frac{1}{C_e}\right) + \frac{1}{q_{max}} \qquad (6)$$

2.3.1.4 Freundlich Isotherm

Another commonly used model for explaining adsorption of heavy metals on clay is the Freundlich model that derived from the Langmuir isotherm, but the difference between Langmuir and Freundlich isotherms in assumption is that in Freundlich isotherm, all surface sites on the adsorbent have the different affinities for different adsorbents[23]. Freundlich equation can be written as in equation (7). To calculate the coefficients $\mathbf{K_F}$ and $\mathbf{n_F}$, equation (7) is linearized as shown in equation (8).

$$q_e = K_F C_e^{1/n_F} \qquad (7)$$

$$\log q_e = \log K_F + \frac{1}{n_F} \log C_e \qquad (8)$$

According to Sawyer et al.[23], Freundlich model indicated that all surface sites on the adsorbent have the equal affinity for adsorbate if the value of 1/n is equal one and when less than one this means decreasing in an affinities with increasing in a adsorption capacity. A summary of various works that have been applied Freundlich, and Langmuir isotherms and their main parameter for Nickel, and Copper as shown in Table 3.

Table 3: Various works that have been applied Freundlich, and Langmuir isotherms for Cu and Ni.

Metal Ions	Constant Conditions			Dosage (g/L)	C range (mg/L)	Isotherm applied	Well fitted	Ref.
	T ^{0}C	Contact Time(min)	pH					
Ni(II)	25	40	7	1-25	100	L,F	L,F	[31]
Cu(II) Ni(II)	20-80	At equilibrium	-	20	50-1000	L,F,LF	L	[32]
Ni(II)	30	180	5.7	2	10-50	L,F	L,F	[33,34]
Ni(II) Cu(II)	30	180 360	5.7	2	10-50	L,F	L,F	[35]
Ni(II)	20-75	150	5.3	10	3-200	L,F	L,F	[36]
Cu(II) Ni(II)	30	360 180	5.7	2	10-250	L,F	L,F	[37]
Cu(II) Ni(II)	30	60	-	25	10-150	L,F	L,F	[38]

L = Langmuir isotherm , F = Freundlich isotherm, and LF = Langmuir Freundlich isotherm

2.3.2 Types of Adsorbents used in Removal of heavy metals

Recently, different adsorbents such as activated carbon, sand, waste tea leaves, eggshell, zeolites, olive stones, clay, wood sawdust[24], chitosan, fly ash, coal and peat moss[39] were used to remove heavy metals from aqueous solution. Due to a large surface area, and the efficiency in removal of heavy metal ions from aqueous solution, activated carbon has been used as adsorbent. However, most of the commercial activated carbon costly[3]. As a result, researchers worked in searching and production for alternative adsorbents to remove heavy metal ions from contaminated water. Due to the valuable properties such as surface area, ion exchange capability, as well as present of the negative charge on the clay minerals structure, clays are considered as an effective alternative to the widely used activated carbon in the removal of heavy metal ions from wastewater[39].

2.3.3 Adsorption of Heavy Metals onto Clay and Bentonite

Recently, several studies have demonstrated the removal of copper and nickel onto clay and bentonite as adsorbent. Alsewailem and Aljlil[32] used a local bentonite clay from Jeddah, Saudi Arabia in removal of Cu and Ni from wastewater under different temperature. And they found that the adsorption capacity increased with rising in temperature. Also, the found that the adsorption capacity of copper on bentonite clay was larger than of nickel where the maximum adsorption capacity at 20 ℃ was 13.22 and 9.29 mg/g for Cu (II) and Ni(II) respectively.

Furthermore in using a local Saudi Arabia adsorbents, Al-sharani, 2012[31] studied the adsorption of nickel on activated bentonite under different conditions such as pH, mass of adsorbent, contact time, and initial concentration. He reported that the local bentonite was an effective and a good adsorbent for removal of Ni (II) from wastewater. Later in 2013 and 2014, he used same adsorbent to remove Fe (II)) and Co(II) respectively from wastewater under various operation parameters[40,41]. Lukman et al, 2013[42] studied the effect of pH of adsorption and desorption of heavy metals in single and multi-component using a local Saudi Arabian clay from Al-Hassa oasis. They found that the initial pH plays an important role in adsorption especially in competitive environment. Koyuncu and Rıza Kul[43] studied the kinetics, and equilibrium adsorption of copper ions by native(NB) and activated bentonite(AAB). They reported that the removal capacity with acid activated bentonite was better than native bentonite under various conditions. Furthermore, they fitted the data to three kinetic models, namely: the intra-particle diffusion, the pseudo–firs -order, and the pseudo-second-order model, and they found that the pseudo–second-order kinetic model was the best fitted model.

Gupta & Bhattacharyya, 2006[33] worked on adsorption of Ni(II) with clays (kaolinite, montmorillonite, and their poly(oxo zirconium) and tetrabutylammonium forms) investigating the effect of different factors such as adsorbent amount, initial ions concentration, shaking time, and pH of solution. The results were showed that the largest adsorption capacity is with montmorillonite, ZrO-montmorillonite, TBA-montmorillonite, kaolinite, ZrO-kaolinite, and TBA-kaolinite respectively.

Furthermore, Gupta & Bhattacharyya[44] also studied the kinetics and thermodynamics of copper adsorption on kaolinite, montmorillonite, and their poly(oxo zirconium) and tetrabutylammonium forms from aqueous phase under different conditions. The results were showed that the largest adsorption capacity is with montmorillonite, TBA-derivative, ZrO- derivative, kaolinite, and TBA-derivative, and ZrO- derivative respectively. In 2008, they also [35], investigated the adsorption of nickel and copper on montmorillonite, kaolinite, and their acid-activated forms from aqueous solution under various conditions and they found that the adsorption capacity of activated montmorillonite , and kaolinite where larger than untreated clays.

Adsorption of copper on Ca-bentonite and Na-bentonite under various conditions such as pH, amount of adsorbent, and adsorbate concentration was reported by Ding et al.[12]. They established that the adsorption capacity with Na-bentonite was greater than Ca-bentonite under various conditions. In 2010, Vieira et al.[36], examined the removal of nickel from aqueous solution by calcined Bofe bentonite clay and factors effecting it (e.g. pH, amount of dosage adsorbent, initial concentration and temperature). And they found that the maximum adsorption capacity was 1.91mg /g at pH 5.3 and the second-order model was the best fitted.

2.4 Clay and Bentonite (Preparation and Characterization)

In the past decades, numerous research works have used clays and bentonite as adsorbent to remove different heavy metals because they have a good ion-exchange capacity and they are regarded as low-cost adsorbents. In reviewed work, researcher cleaned, grinded and sometime treated clays and bentonite before using them as adsorbent. This method called preparation of samples and it differ from one work to another. Alsewailem and Aljlil[32], used a local bentonite clay from Jeddah, Saudi Arabia as adsorbent in removal of copper and nickel from wastewater under different temperature . They characterized the adsorbent by X-ray diffraction (XRD), X-ray fluorescence (XRF), and Brunauer–Emmett–Teller (BET) to determine chemical composition, surface areas, and elemental analysis respectively.

Lukman et al.[42], worked on local Saudi Arabian clay for adsorption and desorption of heavy metals, and to characterize clay, they determined chemical composition by X-ray diffraction (XRD), surfaces, structures, morphologies, and forms of materials by scanning electron microscopy (SEM), surface areas, and pore volume by Nitrogen adsorption (BET), and cation exchange capacities (CEC). In 2014, Koyuncu and Rıza Kul[43], investigated the characterization of native (NB) and acid activated (AAB) bentonite for removal Copper ions from aqueous solution. NB, and AAB bentonite were characterized using X-ray fluorescence (XRF), Nitrogen adsorption (BET), and cation exchange capacities (CEC) to obtain chemical composition, surface areas, and capacity of cation exchange respectively. Table 4 summarizes the characterization for clays and bentonite from previous reviewed works.

Table 4: Characterization techniques, CEC, and surface area for clays and bentonites of reviewed works

Type of Adsorbent	Source	Metal ions	Characterization techniques	Surface Area m^2/g	CEC meq /100g	qe mg/g	Ref.
Bentonite Clay	Jeddah K.S.A.	Cu(II) Ni(II)	XRD, BET, and XRF	62.571	----	13.22 9.29	[32]
Na-bentonite Ca-bentonite	Hebei, china	Cu(II)	XRD, CEC, and for surface area glycol ether	56 20	94.3 60.6	26 12	[12]
K M ZrO-K ZrO-M TBA-K TBA-M	USA	Cu(II)	XRD, CEC, and for surface area Sear's method	3.8 19.8 13.4 35.8 14.2 42.2	11.3 153 10.2 73.2 3.9 47.6	3.9 21 2.6 5.3 2.8 15.1	[44]
K M ZrO-K ZrO-M TBA-K TBA-M	USA	Ni(II)	XRD, CEC, and for surface area Sear's method	3.8 19.8 13.4 35.8 14.2 42.2	11.3 153 10.2 73.2 3.9 47.6	5.18 15.7 3.43 7.43 2.4 6.38	[33]
Acid-activated- K Acid-activate-M	USA	Cu(II) Ni(II)	XRD, CEC, and for surface area Sear's method	15.6 52.3	12.2 341	4.8 21.9 6.6 17.3	[35]
K= Kaolinite, M= Montmorillonite							

2.5 Factors that Affect Adsorption Process

There are many factors effecting on the adsorption process such as contact time, pH of solution, amount of adsorbent, ionic strength, and adsorbate concentration

2.5.1 Effect of Shaking Time

One of the most effective factors on the adsorption process is a contact time between adsorbent and adsorbate, where the uptake of ions continue in an increasing by time until it reach a point of time where the amount of removal is insignificant. This point is called equilibrium time. Several works have studied the effect of contact time on removal of Ni (II) and Cu (II) using clay and bentonite as adsorbent as shown in Table 5.

2.5.2 Effect of Initial Concentration

Removal of metal from the liquid phase on mineral's affected by the initial metal ion concentration, where in most cases the increase of initial concentration leads to increasing capacity of adsorption to equilibrium point[28]. On other hand, increasing initial concentration results in a decreasing of adsorption efficiency. Table 6 shows various works that studied the effect of initial concentration on adsorption metals such as Ni (II) and Cu (II) by clay and bentonite. And the constant conditions are the same which in table 5 with changing in initial concentration and at equilibrium time.

This can be attributed to the fact at higher initial concentration, the ratio of the number available adsorption sites to the number of metal ions is small and thus, increasing in adsorption capacity, decreasing of adsorption efficiency, and the competition for adsorption sites becomes higher[28,33,34,37]. However decreasing in the initial concentration means that increasing in the ratio of the number available adsorption sites to the number of metal ions and consequently, the situation changed and adsorption capacity decreased.

Table 5: Summary of previously reviewed works according equilibrium time.

Type of Adsorbent	Metal ions	Constant Conditions					T_e min	qe mg/g	Ref.
		T ^0C	V mL	C_0 PPm	M g	pH			
Activated bentonite	Ni(II)	25	50	100	0.5	3.2	40	5.5	[31]
Native bentonite activated bentonite	Cu(II)	30	10	25	0.1	6	100	9 16.12	[43]
K M ZrO-K ZrO-M TBA-K TBA-M	Cu(II)	30	-	50	2/L	5.7	360	3.9 21 2.6 5.3 2.8 15.1	[44]
K M ZrO-K ZrO-M TBA-K TBA-M	Ni(II)	30	-	50	2/L	5.7	180	5.18 15.7 3.43 7.43 2.4 6.38	[33]
Acid-activated- K Acid-activate-M	Cu(II)	30	-	50	2/L	5.7	360	4.8 21.9	[35]
	Ni(II)						180	6.6 17.3	
Calcined Bofe bentonite	Ni(II)	20	100	50	1	5.3	150	1.91	[36]

Table 6: Summary of various works that studied the effect of initial concentration (C_0) on adsorption process.

Type of Adsorbent	Metal ions	C_0 range ppm	Highest adsorption		Highest (%) removal efficiency		Ref.
			C_0 ppm	qe mg/g	C_0 ppm	Removal (%)	
Na-bentonite Ca-bentonite	Cu(II)	20-100	100	26 12	20	≈98 ≈95	[12]
Activated bentonite	Ni(II)	20-100	100	5.5	20	≈97	[31]
Calcined Bofe bentonite	Ni(II)	2-200	84.5	2.55	2.66	93.23	[36]
Montmorillonite	Cu(II)	10-50	50	21	10	99.6	[37]
Acid-activated Montmorillonite				21.9		99.9	
Montmorillonite	Ni(II)			15.7		84.3	
Acid-activated Montmorillonite				17.3		91.5	

2.5.3 Effect of Adsorbent Amount

The adsorption capacity and efficiency also affected by the amount of adsorbent added to the solution, and it measure the availability of exchangeable sites. As increased in the amount of dosage the removal rate or adsorption efficiency increased but this with decreasing in the adsorption capacity [12,28,33,36].

Table 7 summarizes various works that investigated the effect of amount of adsorbent on removal metals such as Ni (II) and Cu (II) from liquid phase by clay and bentonite. And the constant conditions are the same which in table 5 with changing in adsorbent amount and at equilibrium time. This mechanism may be attributed to an increasing in the amount of dosage provides an increasing in the surface area of the adsorbent that means an increasing in the number of adsorption sites and consequently, the adsorption efficiency increases[28,33,36,37]. However, decreasing the adsorption capacity is due to two reasons. Firstly; at higher dosage amount, the unsaturation of the adsorption sites reduced as a result, a reducing in the number of sites per unit mass that causing a decreasing in the adsorption capacity. Secondly; a decreasing in the amount adsorbed per unit mass at higher adsorbent amount, this is due to creating a particle aggregation that results in decreasing in the total surface area and increase in diffusional path length[34,36].

Table 7: Summary of various works that have been studied the effect of amount of adsorbent on metals removal.

Type of Adsorbent	Metal ions	M range g/L	Highest adsorption		Highest (%) removal efficiency		Ref.
			M g/L	qe mg/g	M g/L	Removal (%)	
Na-bentonite Ca-bentonite	Cu(II)	0.4-10 2-20	0.4 2	26 12	4 14	100 100	[12]
Activated bentonite	Ni(II)	1-25	1	16	25	94	[31]
Calcined Bofe bentonite	Ni(II)	5-40	5	2.35	40	81.93	[36]
Montmorillonite	Cu(II)	2-6	2	21	6	97.7	[37]
Acid-activated Montmorillonite				21.9		99.3	
Montmorillonite	Ni(II)			15.7		78.3	
Acid-activated Montmorillonite				17.3		85.5	

2.5.4 Effect of pH

The pH factor is recognized as a major parameter effecting on the removal of heavy metals (i.e. Nickel and Copper) from aqueous solutions where at low pH there is a decreasing in adsorption process and increasing as the pH increased[33,35,41,42,44]. Ding Shu-li et al.[12], explained mechanisms that impact the removal of metals by three processes (i.e. ion exchange, adsorption, and precipitation) depend on the changing in pH of solution which agreed with other studied.

In details, there is high number of hydrogen ions H+ at low pH that compete with metal ions (i.e. Nickel and Copper) for adsorption sites and thus decreasing in the amount of adsorbed per adsorbent (q_e) and removal rate[8,33,44,45]. On the other hand, as acidity decreased the adsorption capacity and removal rate (%) increased and this attributed to decreasing H^+ competition with metal ions but the adsorption cannot be done at higher pH (i.e. with Cu at pH>6 and with Ni>8[35,36,37]) due to precipitation of metals.

[CHAPTER 3]

MATERIALS AND METHODS

In this chapter, materials, preparation methods, procedure of experiments, and analysis techniques were discussed in details to achieve the objectives of this study. Figure 1 shows summary of methods and steps that followed in this work to achieve the objectives.

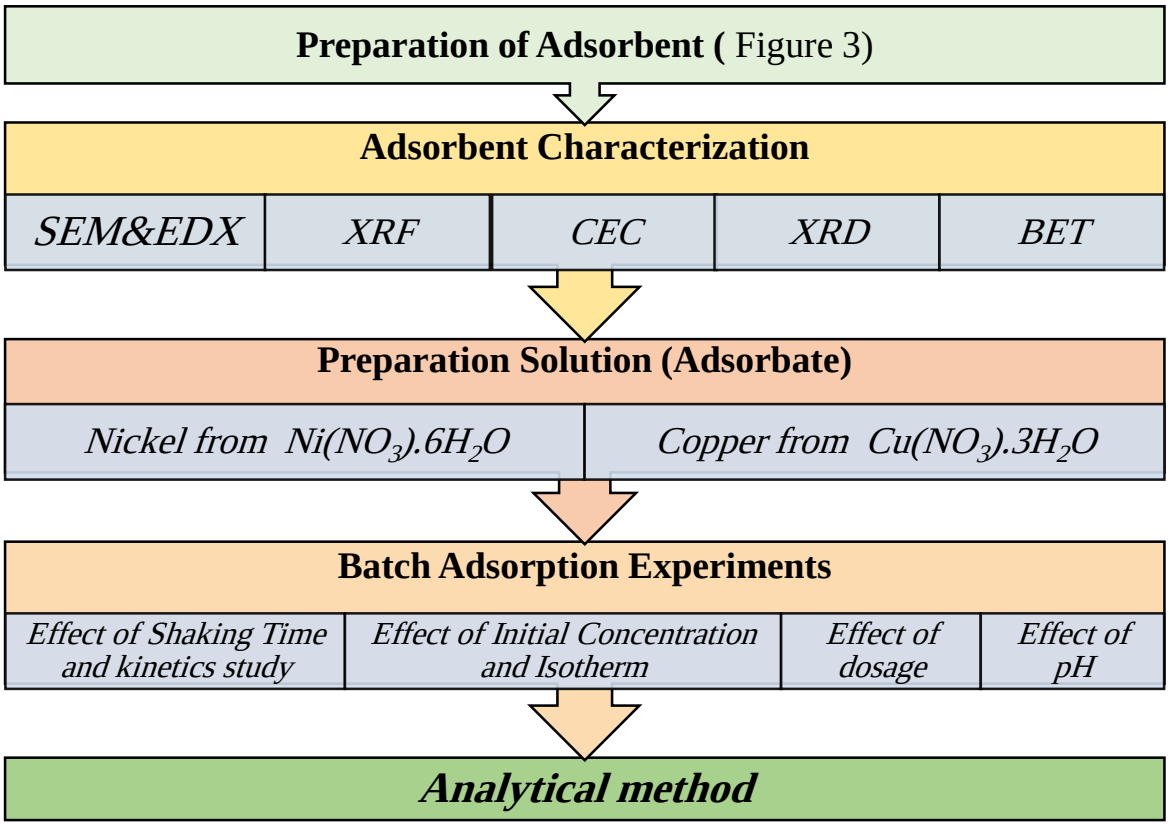


Figure 1: Schematic diagram summarized methods that followed in this work to achieve the objectives

3.1 Preparation of Adsorbents

In this study, Saudi Arabian clay and bentonite were used as adsorbent. The clay was obtained from Al-Hassa city while the bentonite was supplied by Riyadh Geotechnique and Foundations Company. Figure 2 shows the natural clay and bentonite before washing (i.e. in nature). For using these adsorbents in adsorption experimental, clay and bentonite were powdered and sieved through mesh to obtain particles size less than 200 mesh (i.e. 63µm). Because the clay and the bentonite were natural, they treated by 0.1N HNO_3 and the by distilled water DI to remove dust and impurities from adsorbents.

The detailed of treatment clay and bentonite was as following; passing clay and bentonite through 200 mesh were washed by 0.1N HNO_3 each 1 gram by 10 ml. After that, they were dried at 110 ℃ for 24 hours. Next, they were washed by DI water each 1 gram by 10 ml. After that, they were dried at 110 ℃ for 24 hours and then they were grinded. The resulting clay and bentonite were used in the following ratios: 100% Clay, 90% Clay + 10% Bentonite, 70% Clay + 30% Bentonite, 50% Clay + 50% Bentonite, and100% Bentonite. Figure 3 shows a schematic diagram for preparation process of adsorbent.

a

b

Figure 2: Photo of (a) bentonite and (b) clay before washing (i.e. in nature).

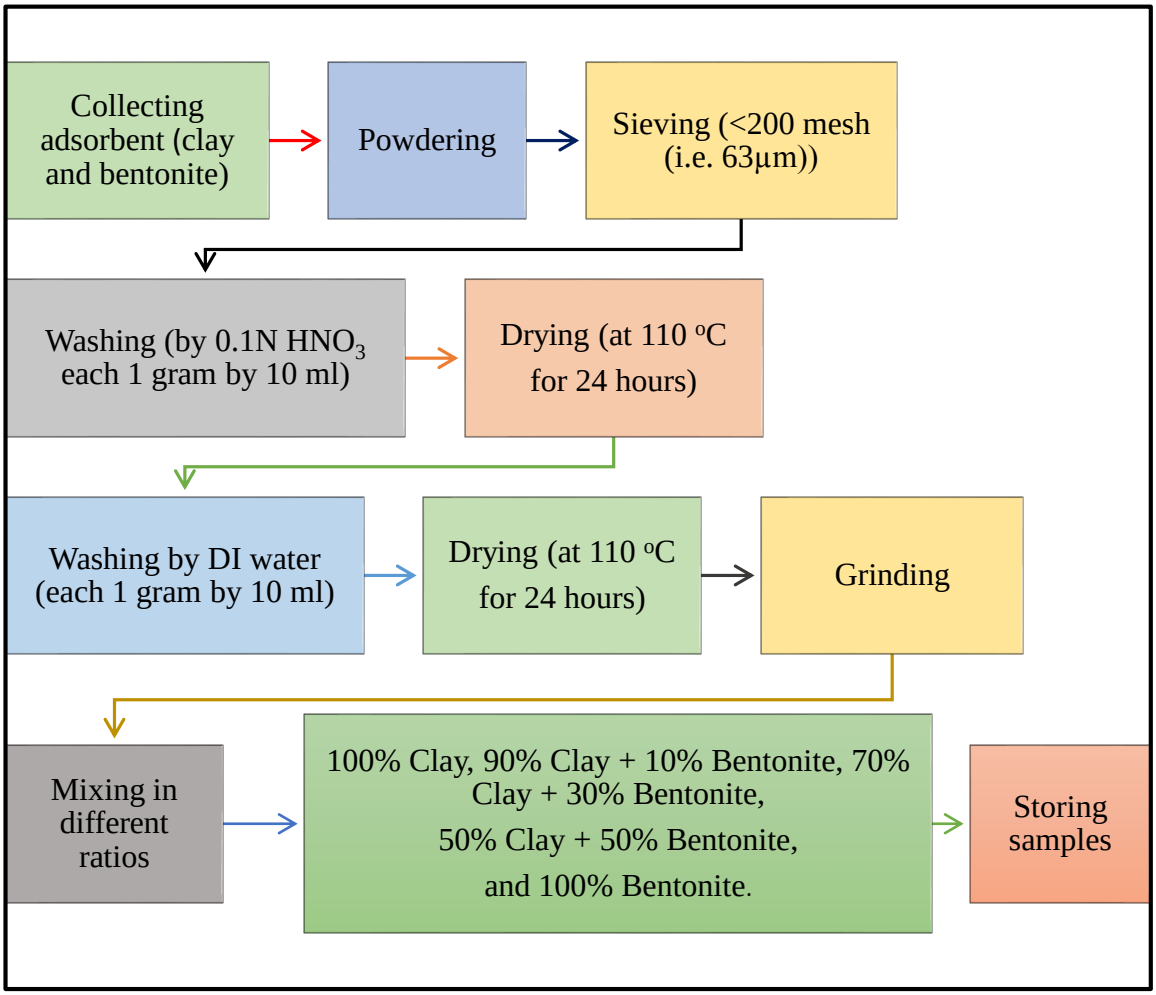


Figure 3: Process flow diagram shows a summary of preparation adsorbents.

3.2 Adsorbents Characterization

To achieve the aims of this study, prepared clay and bentonite were characterized to obtain physical and chemical properties using the following techniques; energy-dispersive X-ray spectroscopy (EDX), scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray fraction (XRF), Brunauer- Emmet-Teller (BET) and cation exchange capacity (CEC). For further information about these techniques are discussed in details in the following subsections.

3.2.1 Energy-dispersive X-ray spectroscopy (EDX), and scanning electron microscopy (SEM)

Clay and bentonite samples were characterized using EDX and SEM to determine microgram scans of samples and to evaluate the chemical compositions. Also, all samples were coated by gold and then interred in scanning microscope (SM-6610LV JEOL with program A2TC Oxford) which has a spectroscopy system through dispersive energy (EDX), to image the samples surface and evaluate of chemical compositions in samples.

3.2.2 X-ray fluorescence (XRF)

In order to identify and quantify chemical compositions of the clay and bentonite, samples of the clay and bentonite were characterized using M4 TORNADO BRUKER micro- XRF.

3.2.3 X-ray diffraction (XRD)

XRD were done with Rigaku Ultima IV MPD X-ray diffractometer using Cu Kα radiation (λ=1.5418 Å) in order to determine the diffractograms of adsorbents clay and bentonite samples.

3.2.4 Brunauer- Emmet-Teller (BET)

Surface area and average diameter for clay and bentonite were measured using the Brunauer- Emmet-Teller (BET) method that is depended on N_2 gas adsorption technique.

3.2.5 Cation exchange capacity (CEC)

The clay and bentonite cation exchange capacity were calculated by EPA 9081 method[46]. In this method, 4 grams of sample (clay or bentonite) were weighted and put in the 50 mL narrow-neck, and round centrifuge tube. And then 33 mL of 1N sodium acetate solution (pH 8.2) was added to the sample. After that the mixed was shaken in a horizontal shaker for 5 min at 120 rpm, and then was centrifuged at 2000 rpm until the supernatant solution is clear for 6 min. After that, the decant solution was thrown and this steps were repeated 3 more times. Then, 33 mL of 99% isopropyl alcohol was added to the sample. Then, the mixed was agitated in a horizontal shaker for 5 min at 120 rpm, and then was centrifuged until the supernatant solution is clear for 6 min at 2000 rpm. Next, the decant solution was thrown and this steps from adding alcohol were repeated 2 more times.

After that, 33 mL of ammonium acetate (pH7) solution was added to the sample. Then, the mixed was agitated in a horizontal shaker for 5 min at 120 rpm, and then was centrifuged until the supernatant solution is clear for 6 min at 2000 rpm. Next, the decant solution was collected into a 100-mL volumetric flask and this steps from adding ammonium acetate were repeated 2 more times. After that, the volume was made up to 100 ml by adding ammonium acetate and the sodium concentration was determined by ICP. Finally, the CEC was calculated be the following equation (9):

$$CEC\,\frac{meq}{100g} = \frac{Na\ ppm * 0.0435 * 10}{weigh\ of\ sample} \qquad (9)$$

3.3 Metal Adsorbate

In this work, all chemicals used were of analytical grade. Standard solution (1000 ppm) of copper was prepared by dissolving 3.7980g of (Cu (NO_3).3H_2O in 250 ml of deionized water and then was mixed slowly by using magnetic stirrer. Next, it was diluted to 1000 ml in a volumetric flask by DI water with continue in mixing. Also, standard solution (1000 ppm) of nickel was prepared by dissolving 4.9530g of Ni (NO_3).6H_2O in 250 ml of DI water and then was mixed slowly by using magnetic stirrer. Then, it was diluted to 1000 ml in a volumetric flask by DI water.

In addition, to prepare required concentration such as 100 ppm, 100 ml of 1000 ppm standard solution was taken and dissolved in 250 ml of DI water and then was mixed slowly by using magnetic stirrer. After that, it was diluted to 1000 ml in a volumetric flask by DI water with continue in mixing. The pH of all standard solutions of copper and nickel were kept below 2 according to the standard method. The pH of stock solutions were adjusted by using 0.1 N HNO_3 or 0.1N NaOH to decrease or increase the pH respectively. Figure 4 shows the pH meter that was used in measurement of the pH of all the solutions in this work.

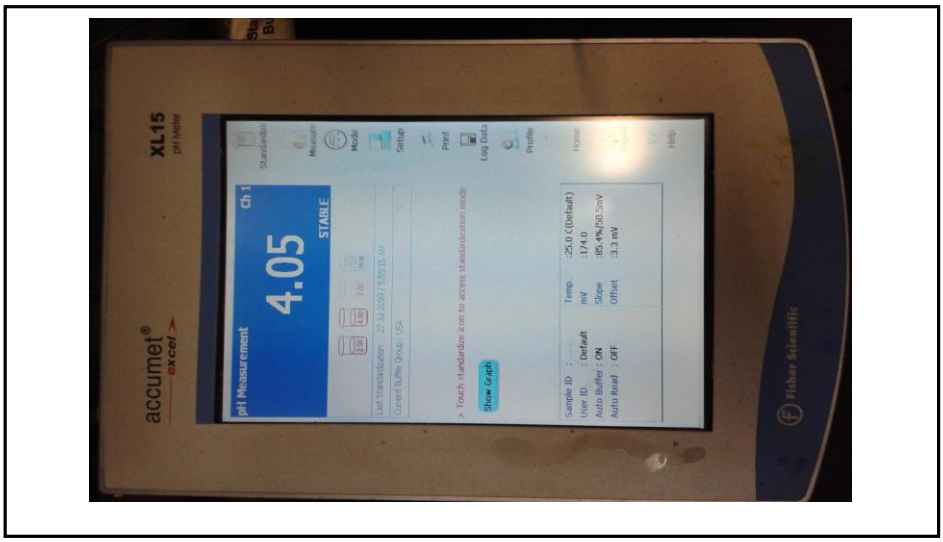


Figure 4: Accumet pH meter.

3.4 Batch Adsorption Experiments

Batch adsorption experiments were conducted on shaker under constant stirring at 200 rpm at room temperature 22 ± 3℃. Also, all experiments were carried out in 125 ml glass bottles containing a constant volume of 50 ml of nickel or copper ions. Figure 5 shows the type of shaker and glass bottle used in this work. For quality control, all samples were tested in duplicate and the mean of them were taken. In addition, blank tests for each work group were carried out without adding adsorbents. Also, all glassware and bottles were immersed in 5% HNO_3 for 48 hr and then washed by dilute 1 N HNO_3. Then, they were rinsed with distilled water and then dried in oven at 110 oC for 24h. To investigate the effect of contact time, the combinations of bentonite - clay, adsorbate concentration, the mass of adsorbent, and the pH of solution, batch adsorption experiments were conducted in four groups.

Figure 5: Shaker and glass which used in experimental.

3.4.1 Effect of Shaking Time and the Combinations of Bentonite - Clay

To determine the effect of shaking time and equilibrium time, experiments were performed at 100 mg/L Cu and Ni concentration, room temperature (22±3^{o}C), pH 5, and 0.2 g of adsorbent (i.e. five mixture ratio each one separately). All experiments were repeated with each mixture ratio. Also, all samples were shaken for a time interval between 0-480 min (5, 10, 15, 30, 45, 60, 120, 240, 360, and 480) for Ni (II) and 0-240min for Cu (II) (5, 10, 15, 30, 45, 60, 120, 180, 240, and 480). After that, samples were taken from shaker and then filtered and prepared for analysis by ICP instrument. Table 8 shows the experimental design for effect of contact time for one mixture ratio of adsorbent (e.g. 50 % clay + 50 % bentonite).

Table 8: Experimental design for effect of contact time and the Combinations of Bentonite - Clay

Variables	Constant conditions					Expected result
Time(min)	Dosage (g)	C_0 (mg/L)	V (ml)	pH	T (^{o}C)	
0-480 for Ni(II)	0.2	100	50	5	22±3	Effect of contact time & Equilibrium time
0-240 for Cu(II)						

3.4.2 Effect of Initial Concentration

The effect of adsorbed concentration and isotherms were studied at different concentration (20, 40, 60, 80, and 100mg/L) and by keeping the amount of clay, solution pH and temperature same as with the kinetics part. But, all experiments were carried out at constant contact time (i.e. equilibrium time that obtained from kinetics part) of 360 min for Ni (II) and 240 min for Cu (II). Table 9 shows the experimental design for effect of initial concentration for one mixture ratio of adsorbent (e.g. 50 % clay + 50 % bentonite).

Table 9: Experimental design for effect of Initial Concentration and Isotherm study.

Variables	Constant conditions					Expected result
Initial Concentration (mg/L)	Dosage (g)	Equilibrium time (min)	V (ml)	pH	T (^{o}C)	
20, 40, 60, 80, and 100	0.2	360 for Ni(II) 240 for Cu(II)	50	5	22±3	Optimum Initial Concentration

3.4.3 Effect of the Amount of Adsorbent

The mass of adsorbents were ranged from 0.2 to 1 gram (0.2. 04, 0.6, 0.8, and1 gram) to investigate the effect of adsorbent. And all parameters were kept constant such as solution concentration (100ppm), shaken time (at equilibrium time 360 min for Ni (II), and 240 min for Cu (II) pH (5) and temperature (22±3^{o}C). Table 10 shows the experimental design for effect of adsorbent dosage for one mixture ratio of adsorbent (e.g. 50 % clay + 50 % bentonite).

Table 10: Experimental design for effect of adsorbent dosage.

Variables	Constant conditions					Expected result
Adsorbent dosage (g)	C_0 (mg/L)	Equilibrium time (min)	V (ml)	pH	T (^{o}C)	
0.2,0.4, 0.6, 0.8, and 1	100	360 for Ni(II) 240 for Cu(II)	50	5	22±3	Optimum adsorbent dosage

3.4.4 Effect of pH

The initial pH of solution was varied from 3.5 to 8 (3.5, 5, 6.5and 8) to study the effect of pH on removal of both copper and nickel ions. In this part, all experiments were carried out under constant condition of contact time (at equilibrium time 360 min for Ni (II), and 240 min for Cu (II)), initial solution concentration (100ppm), temperature (22±3^{o}C), and adsorbent amounts (0.2 gram). Table 11 shows the experimental design for effect of pH on adsorption capacity for one mixture ratio of adsorbent (e.g. 50 % clay + 50 % bentonite).

Table 11: Experimental design for effect pH.

Variables	Constant conditions					Expected result
pH	Dosage (g)	Equilibrium time (min)	V(ml)	C_0 (mg/L)	T (^{o}C)	
3.5, 5, 6.5 and 8	0.2	360 for Ni(II) 240 for Cu(II)	50	100	22±3	Optimum pH

3.4.5 Analytical Method

After adsorption processes, all samples were filtered through a 0.45 μm membrane filter using syringe filter and then the filtrated samples were collected and kept in bottles. Before, analysis samples by inductively coupled plasma (ICP), they were diluted to 1 ppm for analyzing by ICP. Then, ICP calibration was established by measuring the known concentrations of standard solutions and making calibration curves. The calibration samples concentration were ranged from 0.2 ppm to 2 ppm (0.2, 0.5, 1, and 2 ppm). 2 % HNO_3 standards and 5 % HNO_3 blank that were used for initial calibration verification (ICV), Re-slope, continuous calibration verification (CCV), and checking[42]. Finally, all samples that were diluted to 1 ppm or less than one ppm were analyzed using inductively coupled plasma (ICP). Figure 6 shows inductively coupled plasma (ICP) which were used in analysis unknown samples.

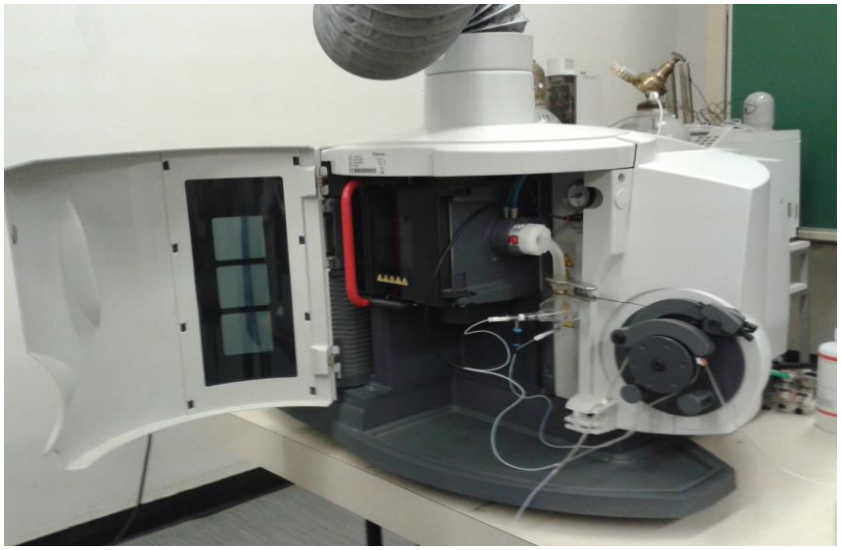


Figure 6: Inductively coupled plasma (ICP)

3.5 Analysis of Adsorption data

To study the adoption capacity, kinetics, and Isotherms, the concentrations of heavy metals that adsorbed to adsorbents were determined. And to determine heavy metals removal, equation (10) was used using the data obtained from ICP analysis.

$$C_{adsorbed} = C_0 - C_{remaining} \qquad (10)$$

3.5.1 Adsorption Capacity

The amount of heavy metal ions uptake (adsorbate) per unit mass of solid (adsorbent) is called the adsorption capacity (q)and it was calculated using equation (11) [42]. At equilibrium time, the maximum adsorption capacity (q_e) is the maximum of heavy metals removed per unit mass of adsorbent which was determined by equation (12).

$$q = \frac{C_0 - C_{adsorbed}}{M} * V \qquad (11)$$

$$q_e = \frac{C_0 - C_e}{M} * V \qquad (12)$$

3.5.2 Kinetics Study

Kinetics study for copper and nickel were undertaken at constant conditions of pH 5, amount of adsorbent 0.2g, and initial concentration 100 mg/L using different shaken time between 0-240 min, and 0-360 min for copper and nickel respectively. Two kinetics models were employed which are pseudo first order and pseudo second order models and to determine the parameters of these models plots of ($Ln(q_e - q_t)\ VS.t$) and ($t/q_e\ VS.t$) were plotted.

3.5.3 Isotherms Study

The adsorption isotherms for copper and nickel on bentonite and clay were determined at equilibrium time, and constant conditions of pH 5, amount of adsorbent 0.2g, at different initial concentrations (0-100 mg/L). As presented in the previous chapter, two models; Langmuir and Freundlich isotherms were fitted by plotting ($1/q_e\ VS.1/C$) and ($Log\ q_e\ VS.Log\ C$) respectively. From these plots and using equations 5 and 8, the models parameters and plots correlation coefficients were calculated. In addition, the dimensionless equilibrium parameter for Langmuir isotherm R_L was calculated using the following equation (13):

$$R_L = \frac{1}{1 + K_L * C_0} \qquad (13)$$

If: $0 < R_L < 1$ the adsorption is favorable, $R_L > 1$ the adsorption is unfavorable, $R_L = 1$ the adsorption is linear, and $R_L = 0$ the adsorption is irreversible[36].

[CHAPTER 4]

RESULT AND DISCUSSION

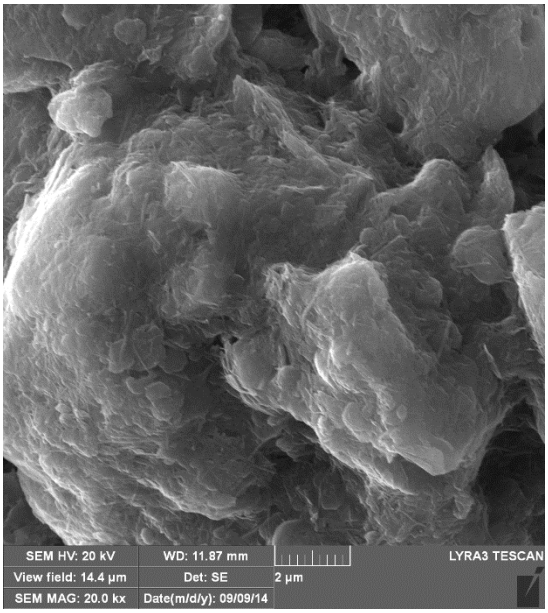
In this chapter, the results obtained from experimental work will be presented and discussed in details. These include characterization of the clay and bentonite, single adsorption for copper and nickel studies and the factors effecting the adsorption process, Isotherms study, and kinetics study.

4.1 Characterization of Adsorbents

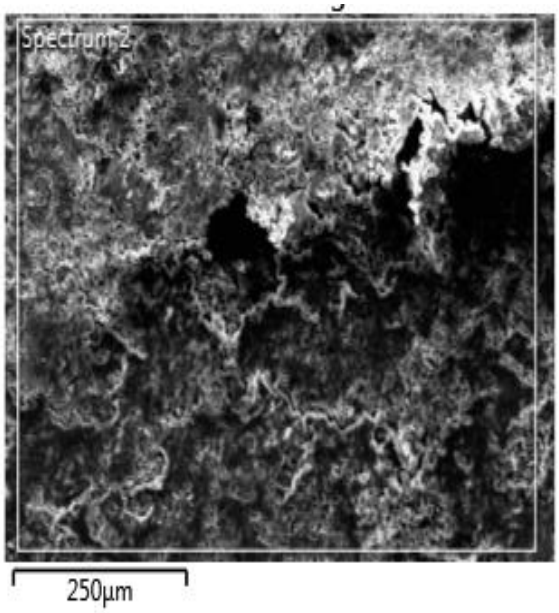
In this part of this section, the physical, chemical, mineralogical characterization of clay and bentonite are discussed as follows:

4.1.1 Morphology and Chemical Characterization by SEM and EDX

To determine forms, micrograph scans, and surface structure of clay and bentonite the scanning electron microscopy (SEM), was used. This picture captured by the SEM can be seen in Figure 7(A - D for clay and bentonite) at high and low resolution. Figure 7, clearly shows that there is a marked differences in surface structure and morphology between clay and bentonite.



A



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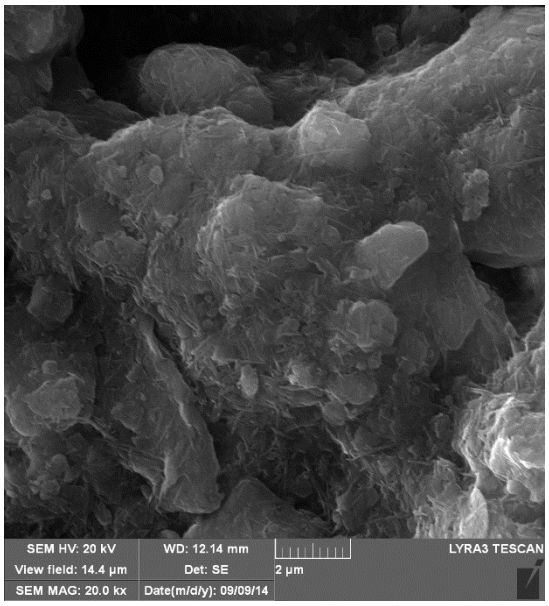

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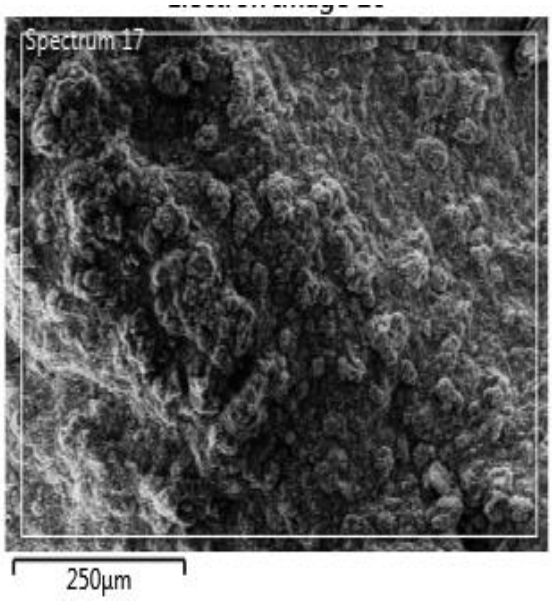


D

Figure 7: Scanning electron microscopy (SEM) A) clay at high resolution B) clay at low resolution C) bentonite at high resolution D) bentonite at low resolution.

Also, the energy-dispersive X-ray spectroscopy (EDX) was used to determine the elemental composition of samples of the clay and bentonite. The result shows that the main dominant elements for both clay and bentonite are O and Si with values respectively of 51.8 and 19.8 for clay and 42.8 and 25.1 for bentonite. Also, elements of Al, Ca, Fe, Mg, and Ti present lesser quantities for both clay and bentonite and Na, K only in clay.

4.1.2 Chemical Composition by X-ray fluorescence (XRF)

Because EDX technique has low accuracy for determining the elemental composition of samples, X-ray fluorescence was performed for some samples before and after adsorption. This was carried out using M4 TORNADO BRUKER micro- XRF in order to identify and quantify chemical compositions of the clay and bentonite and the results are presented in table 12. Apparently the main dominant elements in the clay are Ca followed by Si and Fe while in the bentonite Fe and Si followed by Al and Ca. In addition, the ratio of Si/Al in bentonite (3.24 %) is more than in clay (2.7%).These characteristics of the clay and bentonite are greater extent similar to clays characterized by other researchers. As Jarrah, 2009[47] reported that the exchange capability increase as decreasing in the ratio of Si/Al. Closed findings were reported by other researchers using different clays. Al-Shahrani, 2012 [31] used activated bentonite as adsorbent to remove nickel and found that the activated bentonite composed from Si, Al, Fe, Ti, Mg, Na, Ca, K, and Mn where the main dominant elements are Si, and Al and the ratio of Si/Al is 5.2. Also, Aljlil and Alsewailem, 2014[32] studied the adsorption of copper and nickel using bentonite clay from Jeddah and reported that the main dominant elements in bentonite clay are Si and Al and the ratio of Si/Al is 2.7.

Table 12: Chemical composition in clay and bentonite by X-ray fluorescence (XRF)

Component	Clay (Wt %)	Bentonite (Wt %)
Si	26.44	39.57
Al	9.76	12.2
Ca	40.15	4.24
Fe	12.5	39.61
Ti	0.6	2.17
K	4.18	
Mg	2.34	
Na	4.04	
Si/Al	2.709	3.2434

4.1.3 BET Surface area, Cation exchange capacity, and other physical properties

Table 13 shows some physical properties of clay and bentonite obtained from numerous analysis technique as discussed in the experimental section. As shown in the table the surface area of bentonite is almost twice that of the clay. Also, the average diameter particles in clay is larger than in the bentonite. In addition, bentonite has CEC five times that of the clay. As a result, bentonite is better than clay in the aforementioned physical properties. However, clay is better than bentonite in the natural pH which is considered as a major parameter effecting the removal of heavy metals where the values of pH are 5.5 with clay and 4 with bentonite[42].

These characteristics of the clay and bentonite are greater extent similar to clays characterized by other researchers. Aljlil and Alsewailem, 2014 [32] studied the adsorption of copper and nickel using bentonite clay from Jeddah and found that the BET surface area of bentonite clay is 62.5671 m^2/g and the average pore diameter is 95.650 Å. Bertagnolli et al, 2011[48] investigated the removal of copper by bentonite clay and found that the BET surface area is 25.34 m^2/g. Also, Lukman et al, 2013[42] worked on removal of different metals using clay and found that the BET surface area of bentonite clay is 42.13 m^2/g.

Table 13: Physical properties of clay and bentonite.

Property	Value for Clay	Value for Bentonite
Specific gravity (ASTM D 854)	2.65	2.77
BET (Branaur-Emmett-Teller) Specific surface area, m^2/g	20.83	44.2775
Average Diameter nm	112.8203	61.5496
Passing through sieving No.	200	200
CEC meq/100g (EPA 9081)	20.9	101.3
pH (ASTM D 4972)	5.5	4

4.1.4 X-ray diffraction (XRD) Results

In order to determine the diffractograms of adsorbents clay and bentonite samples, the X-ray diffraction (XRD) were done using Rigaku Ultima IV MPD X-ray diffractometer with Cu Kα radiation (λ=1.5418 Å). Figure 8 shows the XRD pattern for clay where the clay is mainly composed of calcite [$Ca(CO_3)$], glauconite [$(K, Na)(Fe, Al, Mg)_2(Si, Al)_4O_{10}(OH)_2$], and quartz-alpha low [SiO_2]. On the other hand, the XRD analysis for bentonite shows that the bentonite is mainly composed of Magnetite [Fe_3O_4], quartz low HP [SiO_2], portlandite HP [$Ca(OH)_2$] as shown in figure 9. Lukman et al, 2013[42] worked on removal of different metals using clay and found that the clay composed of montmorillonite; quartz and calcite. Also, Aljlil and Alsewailem, 2014[32], used bentonite clay from Jeddah as adsorbent and reported that it composed of Kaolinite (9%), montmorillonite 82 %), quartz and illite (9%).

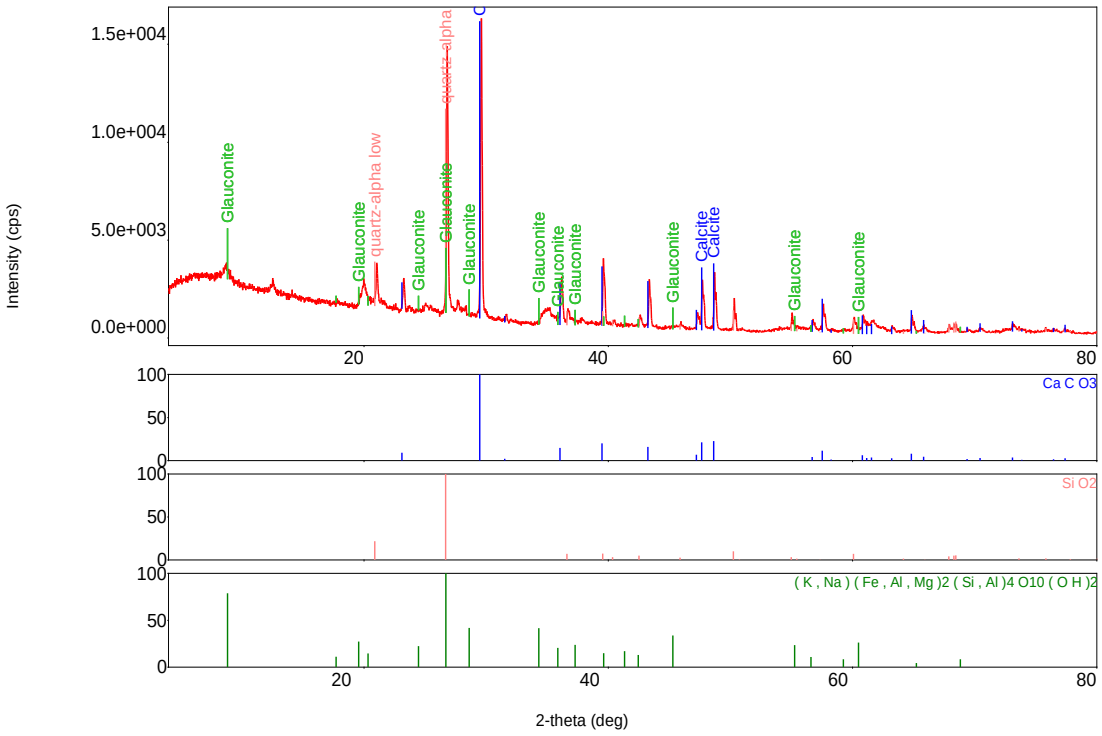


Figure 8: XRD analysis for clay.

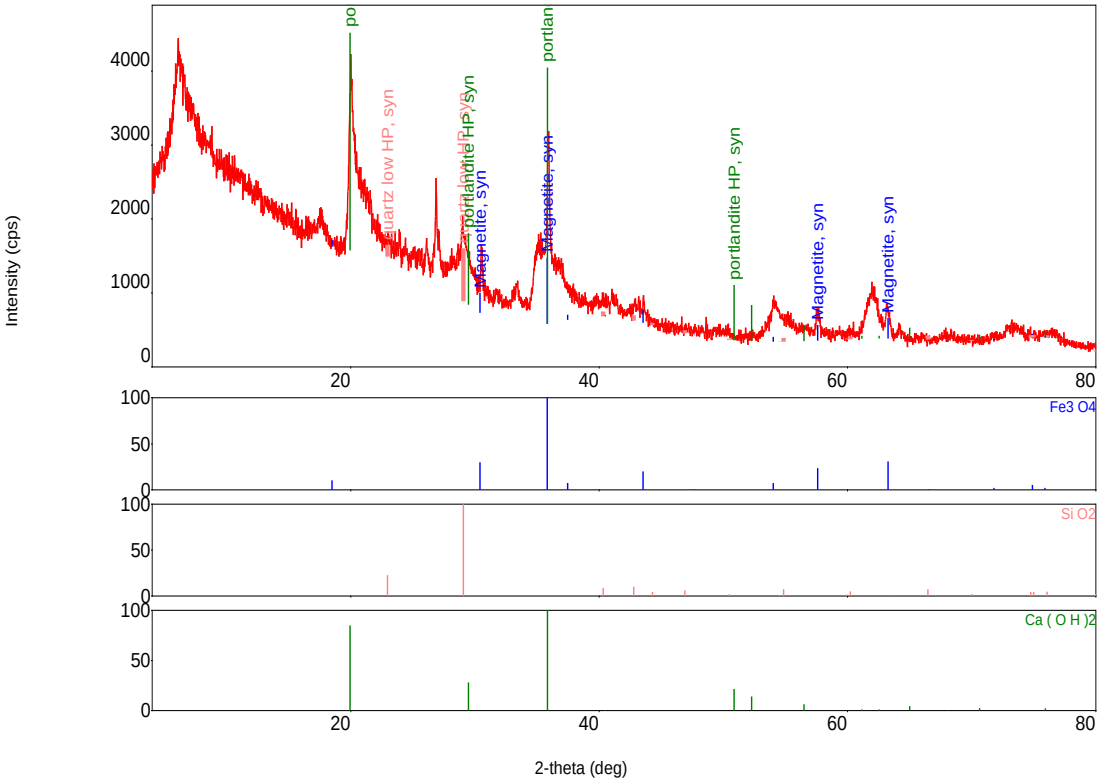


Figure 9: XRD analysis for bentonite.

4.2 Single Adsorption of Copper and Nickel onto Bentonite, the Combinations of Bentonite-Clay, and Clay alone

All experiments were take place in 125 ml glass bottles containing a constant volume of 50 ml of nickel or copper solution. In addition, the adsorption experiments were performed in four groups to examine the effect of shaking time, initial concentration, the amount of adsorbent, and pH of solution. Also, the kinetics study and isotherms were applied to the results obtained from adsorption of copper and nickel to fit the best model to the experimental data.

4.2.1 Factors Affect Copper and Nickel Removal

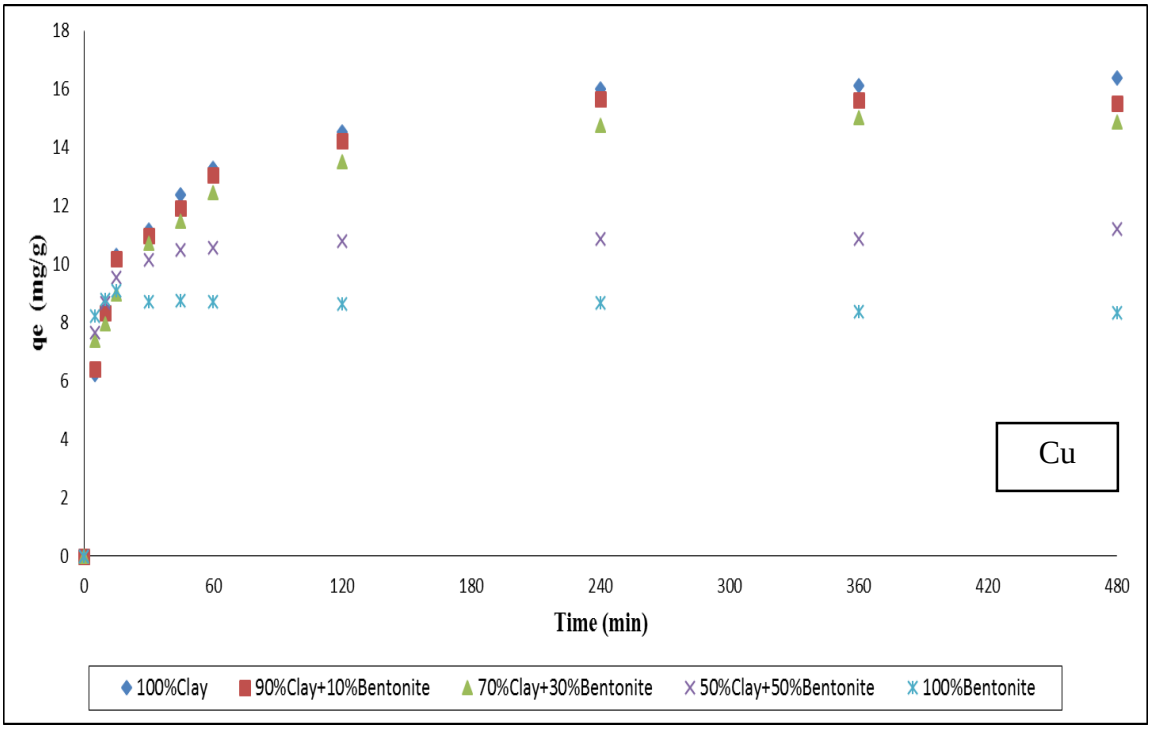
The removal of copper and nickel from wastewater using clay and bentonite as adsorbents was affected by different factors such as shaking time, metal concentration, and others. In this study, the adsorption of Cu and Ni was investigated with studying four factors: shaking time, initial concentration, the amount of dosage, and pH.

4.2.1.1 Effect of Shaking Time and the Combinations of Bentonite - Clay

The effect of contact time on the removal efficiency and adsorption capacity of copper and nickel ions was investigated where the shaking time was ranged from 0 to 480 min (5, 10, 15, 30, 45, 60, 120, 180, 240,360, 480), under constant condition of initial concentration

of 100 mg/L, mass of adsorbent of 0.2 g, solutions pH at 5, 200 rpm of agitation Speed, and temperature of (22±3^{o}C).Also, the effect of the combinations of bentonite-clay on removal efficiency as well as adsorption capacity of copper and nickel ions was studied using five different mixture ratio as following 100% Clay, 90% Clay + 10% Bentonite, 70% Clay + 30% Bentonite, 50% Clay + 50% Bentonite, and100% Bentonite.

Figures 10, and 11 show that the effect of contact time and the combinations of bentonite-clay on removal efficiency and adsorption capacity of copper and nickel. The result showed that the equilibrium was established at 30 min and 45 min with 100 % bentonite, and 240 min and 360 min with 100% clay for copper and nickel respectively. Table 14 shows the maximum removal efficiency and adsorption capacity of copper and nickel for different mixture ratio of bentonite-clay at equilibrium time. From figures 10, and 11 apparently the removal efficiency as well as the adsorption capacity of copper and nickel were very fast in the first few minutes and then decreased until the equilibrium was reached. Jiang, et al, 2010,[38] also, Bhattacharyya and Gupta, 2006 [44] reported that this increment may be attributed to the increase in agitation time which results in decreasing in the adsorption sites on adsorbents which were gradually filled up by metal ions and the kinetics become dependent on the metal ions were transported from the bulk liquid phase to the actual adsorption sites.



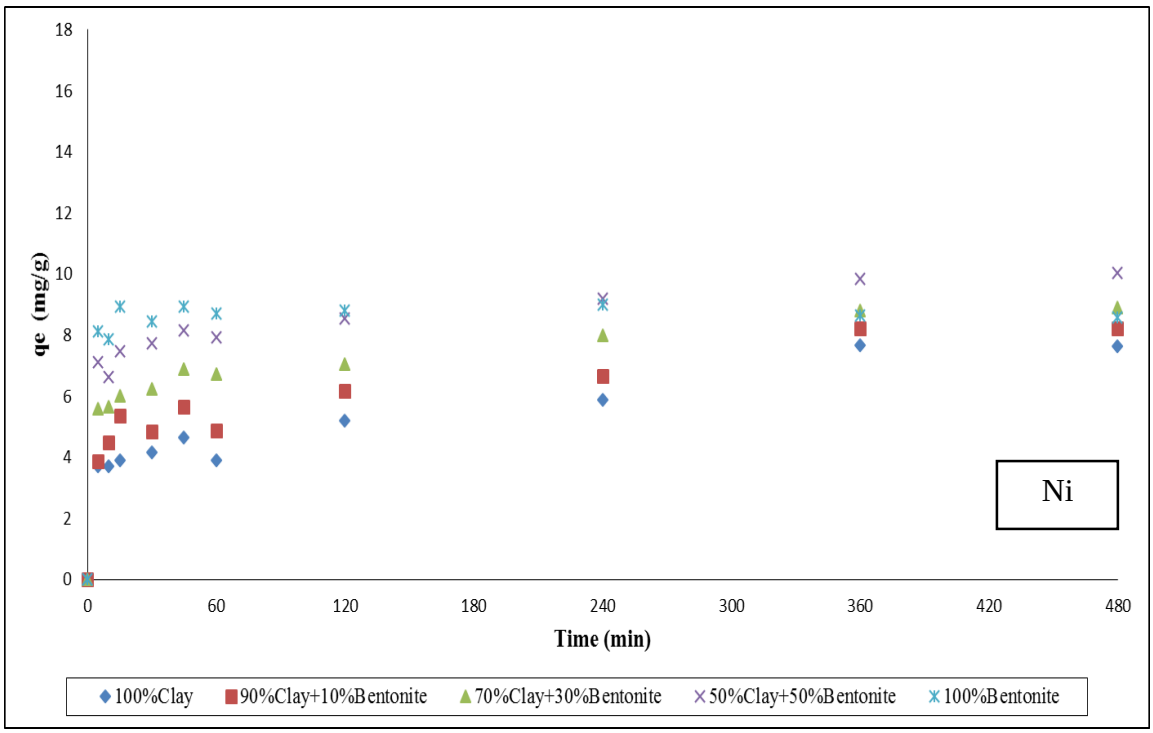


Figure 10: The effect of shaking time on adsorption capacity for copper and nickel onto different mixture ratio of clay and bentonite.

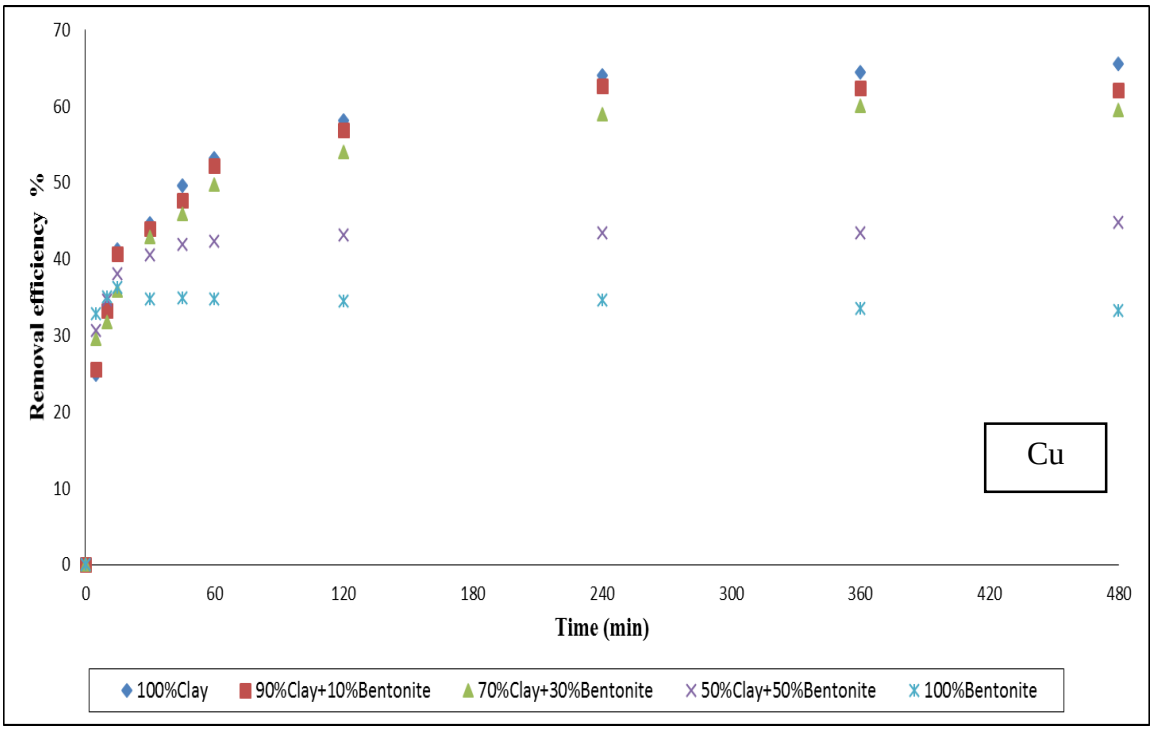
This effect of contact time on adsorption capacity and removal efficiency of copper and nickel onto different clays as adsorbent was found by other researchers. Bhattacharyya and Gupta, 2006 and 2008[35,44] also, Liu and Zhou,2010[49] studied the removal of copper and nickel on different clays and found that the removal efficiency as well as the adsorption capacity of copper and nickel was very fast in the first few minutes and then decreased until the equilibrium had been reached. Where the equilibrium was reached after 200 min for copper and nickel according to Liu and Zhou,2010[49], after 240 min for copper according to Bhattacharyya and Gupta, 2006 Bhattacharyya and Gupta, 2006[44], and after 360 min for copper and 180 min for nickel according to Bhattacharyya and Gupta, 2008[35].

Also, from figures 10, and 11 it can be observed that as increasing in the ratio of bentonite to clay the adsorption capacity and removal efficiency decreased with copper while increased with nickel. Table 14 shows the maximum removal efficiency and adsorption capacity of copper and nickel for different mixture ratio of bentonite-clay at equilibrium time. In other words, the removal of copper on clay (64 %) is more than on bentonite (34.85 %) almost twice. Conversely, with nickel reverse is the case as the removal of nickel on clay (30.7 %) is slightly lower than on bentonite (35.7 %). This may be attributed to the combined district differences of physical and chemical of both adsorbate and adsorbent.

Table 14: The maximum removal efficiency % and adsorption capacity of copper and nickel for different mixture ratio of bentonite-clay at equilibrium time.

Mixture ratio of adsorbent	Copper			Nickel		
	Te (min)	q_e (mg/g)	Removal efficiency %	Te (min)	q_e (mg/g)	Removal efficiency %
100% clay	240	16	64	360	7.7	30.7
90% clay + 10% bentonite	240	15.6	62.6	360	8.2	32.9
70% clay + 30% bentonite	240	14.7	59	360	8.8	35.3
50% clay + 50% bentonite	120	10.8	43.2	360	9.8	39.3
100% bentonite	30	8.7	34.85	45	8.9	35.7

Futalan et al, 2011[50] studied the adsorption of copper, lead, and nickel onto chitosan-coated bentonite and reported that the removal effected by the electronegativity of metal ions where the attraction between two atoms increased as their electronegativity difference increased. Bohli, 2013 [51] studied the adsorption of cadmium, copper, lead, and nickel on olive stones and reported that the removal effected by some chemical characteristics of the metal ions such as ionic radius of metals and hydration energy. Ziyath et al, 2011[52] reviewed the effect of physical and chemical parameters on removal of heavy metals by zeolite and reported that the removal effected by properties of zeolite such as Si/Al ratio and surface area and physico-chemical conditions of the system such as pH of solution. Koppelman and Dillard, 1997[53] studied the adsorption of copper and nickel on different clays and reported that the removal of metals influenced by the initial and final pH of solution.



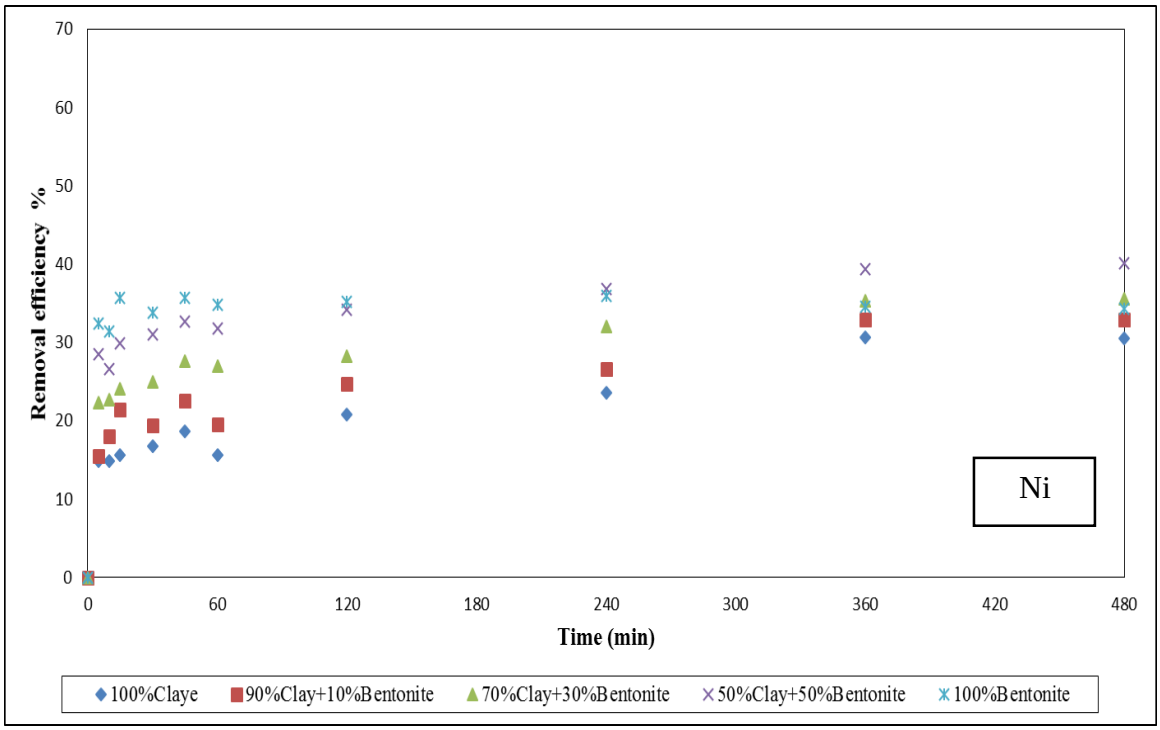
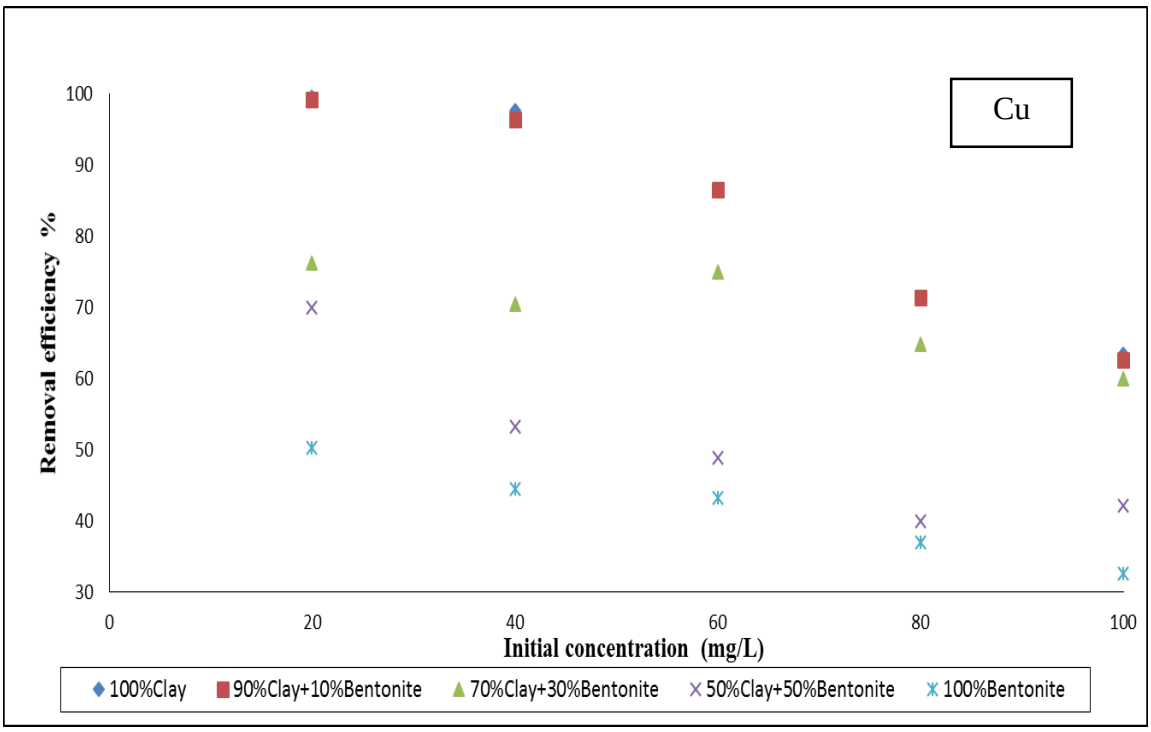


Figure 11 : The effect of shaking time on removal efficiency % of copper and nickel using different mixture ratio of clay and bentonite.

4.2.1.2 Effect of Initial Concentration

Figures 12, and 13 show the effect of initial metal ions concentration on removal of copper and nickel from aqueous solution with clay, bentonite and their different combinations. This was investigated at constant conditions of 200 rpm, pH 5, temperature of (22±3^{o}C), mass of adsorbent of 0.2 g, and at equilibrium time of 240 min and 360 min for copper and nickel respectively where the initial concentration was ranged from 20 to 100 ppm (20, 40, 60, 80, and100 ppm).

The results from figure 12 show that, the removal efficiency decreased with an increasing in the initial metal concentration of Cu and Ni for all adsorbents; bentonite, the combinations of bentonite-clay, and clay alone. Table 15 shows the maximum removal efficiency and adsorption capacity of copper and nickel with different initial concentration for all adsorbents at equilibrium time. Vieira et al, 2010[36], and Jiang et al, 2010[38] studied the effect of initial concentration on removal efficiency, and found similar trends. Also, they reported that this decrement in removal efficiency may be attributed to the increase in the ratio of the number metal ions in solution to the available number of adsorption sites as the initial metal ions increase in solution and consequently, a competitive environment was created.



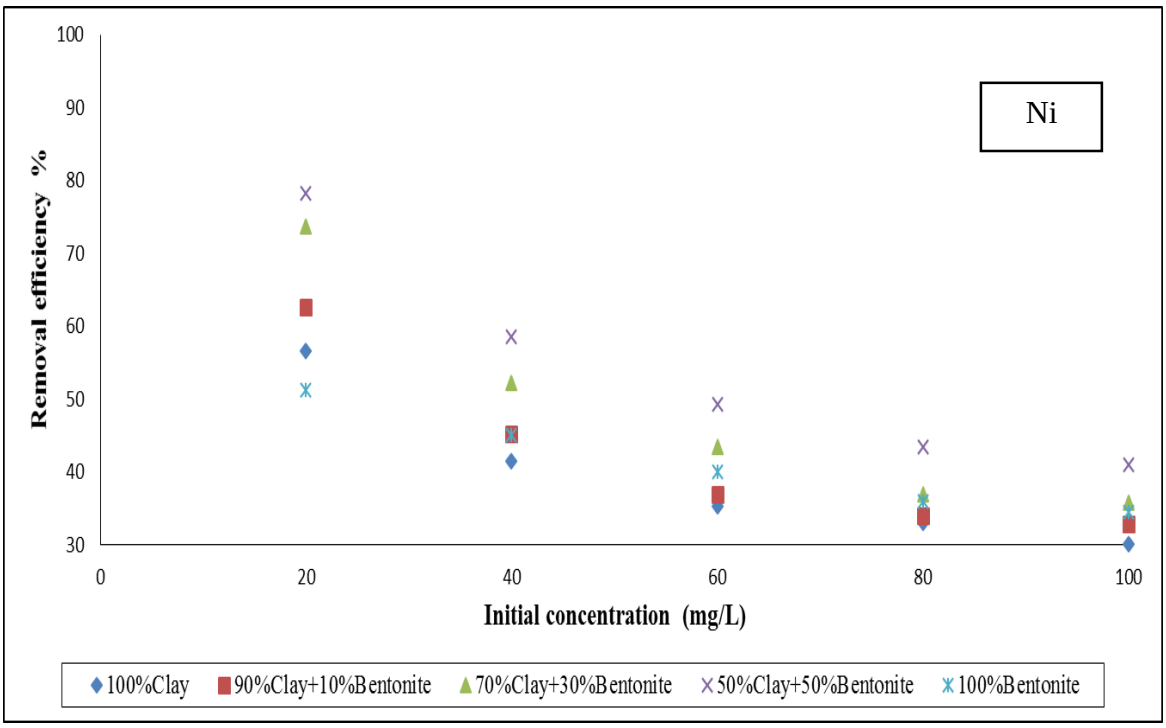
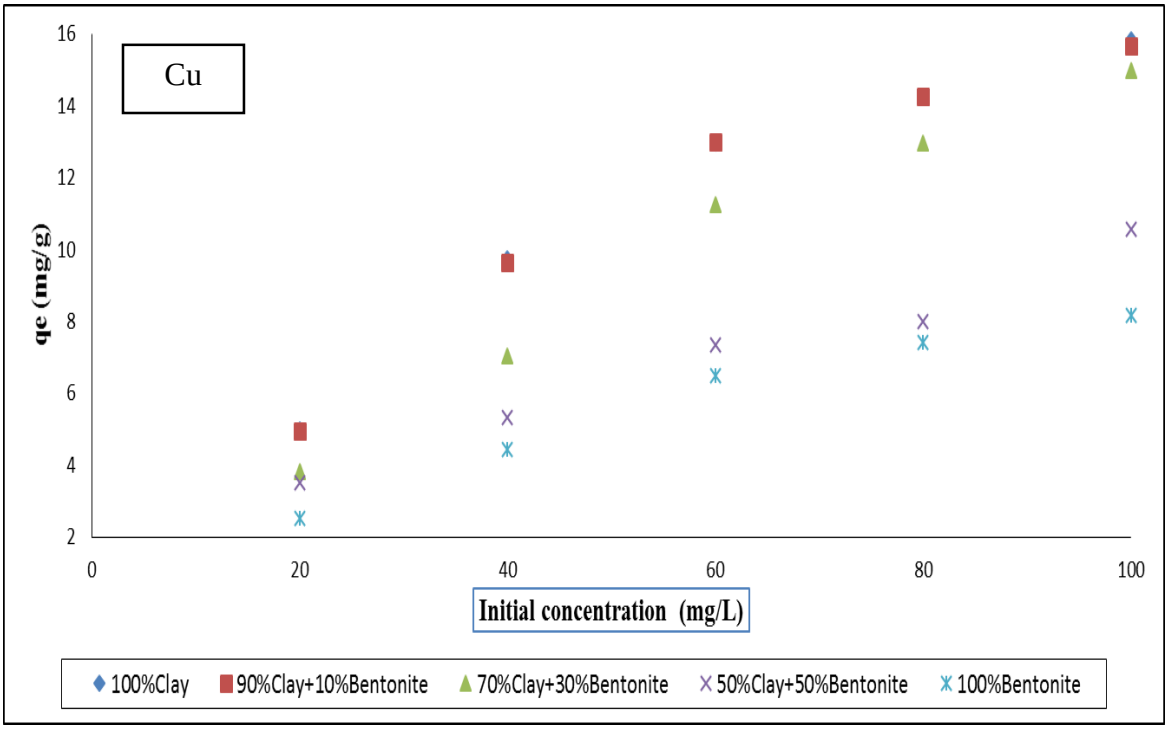


Figure 12: The effect of initial concentration on removal efficiency % of copper and nickel using different mixture ratio of clay and bentonite.

Table 15: The maximum removal efficiency % and adsorption capacity of copper and nickel with different initial concentration for all adsorbents at equilibrium time.

Mixture ratio of adsorbent	C_0 mg/L	Copper		Nickel	
		q_e (mg/g)	Removal efficiency %	q_e (mg/g)	Removal efficiency %
100% clay	20	4.97	99.47	2.83	56.6
	100	15.84	63.38	7.51	30
90% clay + 10% bentonite	20	4.96	99.21	3.1	62.6
	100	15.65	62.6	8.2	32.9
70% clay + 30% bentonite	20	3.8	76.1	3.68	73.7
	100	14.97	59.9	8.9	35.7
50% clay + 50% bentonite	20	3.5	69.9	3.9	78.2
	100	10.5	42.2	10.2	40.9
100% bentonite	20	2.5	50.2	2.56	51.2
	100	8.2	32.7	8.63	34.5

However, at the equilibrium the adsorption capacity for copper and nickel (figure 13) increased with increasing in the initial metal concentration for the different combinations of bentonite and clay. Tan & Ting, 2014[54] studied the effect of initial concentration on adsorption capacity, and found similar trends. Also, they reported that this trend may be attributed to the increased in the number of metal ions to adsorbent sites resulting increase in the chance of interaction between metal ions and soil particles as a result, an increase in adsorption capacity at high metal ions concentration. Similar findings were reported by other researchers who studied the effect of initial concentration on removal of copper and nickel by different clays as shown in table 6.



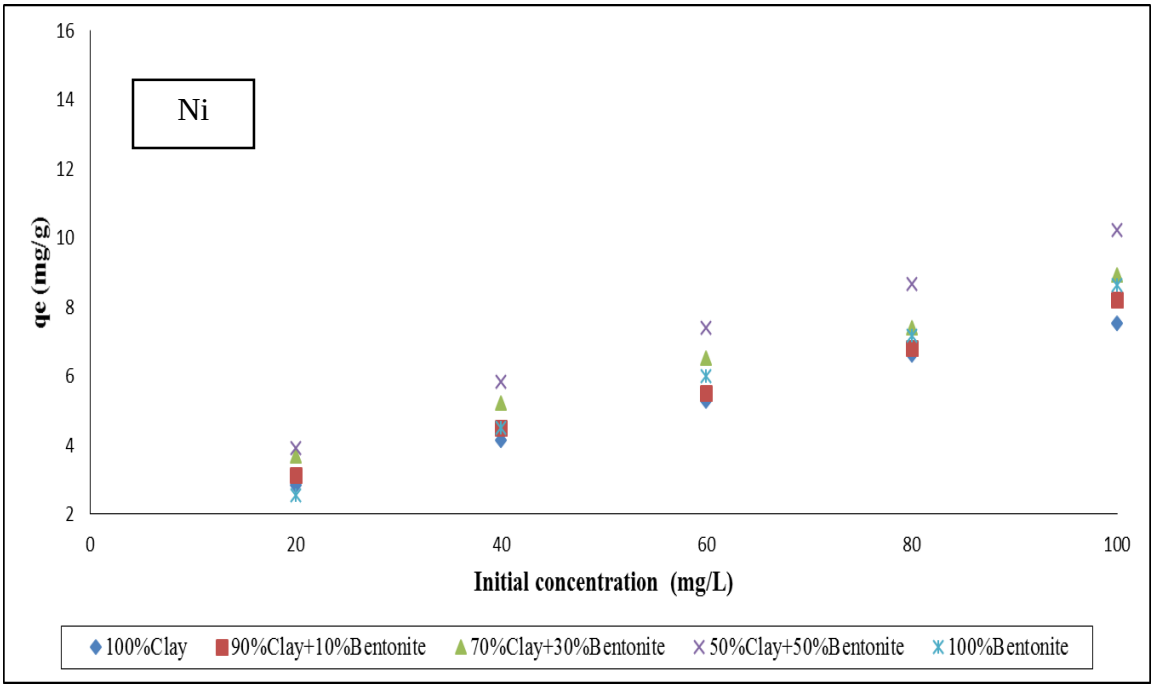
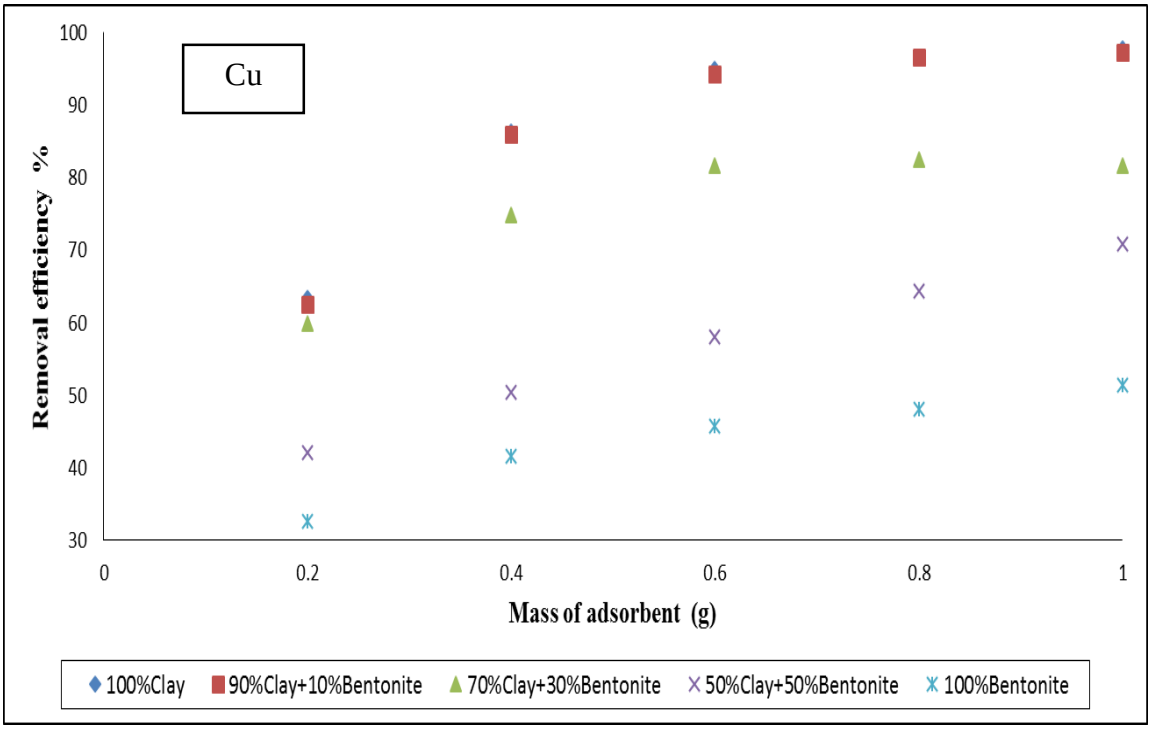


Figure 13: The effect of initial concentration on adsorption capacity for copper and nickel onto different mixture ratio of clay and bentonite.

4.2.1.3 Effect of the Amount of Adsorbent

The effect of the amount of adsorbents on adsorption of copper and nickel by clay, bentonite and their combinations was examined under constant conditions of contact time of 240 min and 360 min (at the equilibrium) for copper and nickel respectively at 200 rpm, initial concentration of 100 mg/L, solutions pH at 5, and temperature of (22±3^{o}C) where the mass of adsorbents were changed from 0.2 to 1 gram (0.2, 0.4, 0.6, 0.8, and1 gram).

As shown in figure 14, for all the adsorbents types; bentonite, the combinations of bentonite-clay, and clay alone demonstrated that the removal efficiency increased as more amount of the adsorbents were used. Table 16 shows the maximum removal efficiency and adsorption capacity of copper and nickel with different adsorbent mass for all adsorbents at equilibrium time. Ding et al, 2009[12], and Zhang, & Yuan, 2012[55] studied the effect of the amount of adsorbent on metals removal, and found similar trend. Also, the reported that this increase in removal efficiency may be attributed to the increased in exchangeable sites and surface area which receive more ions to their surfaces as increased in adsorbent amounts at a fixed initial concentration of metal ions.



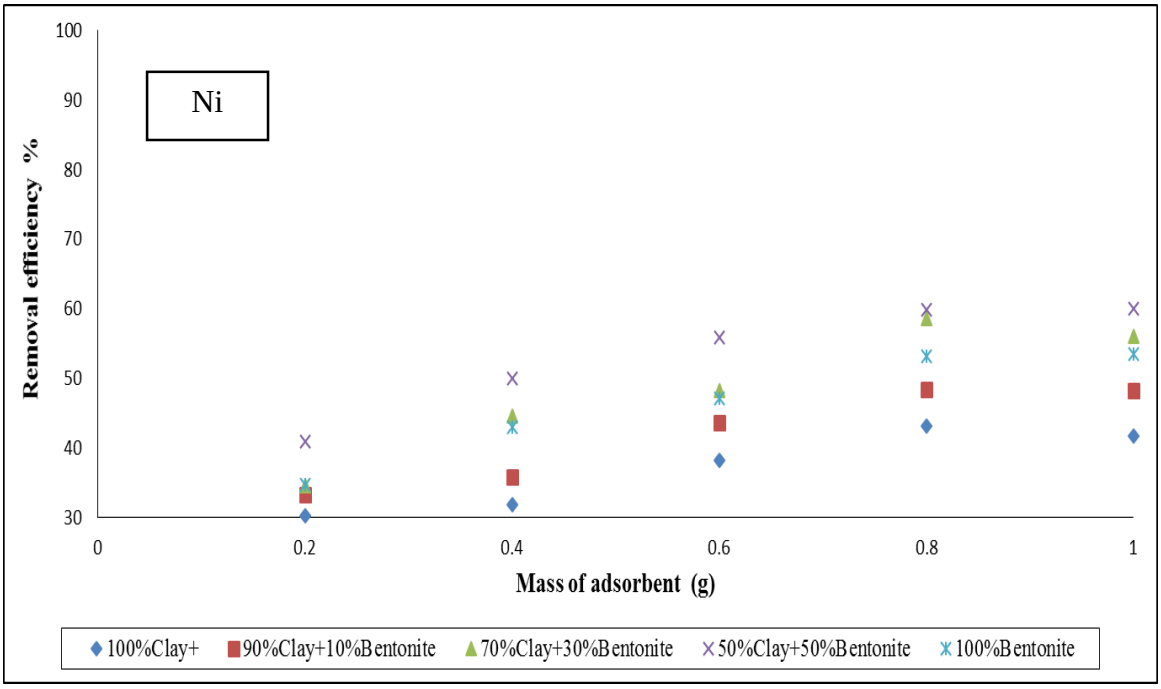
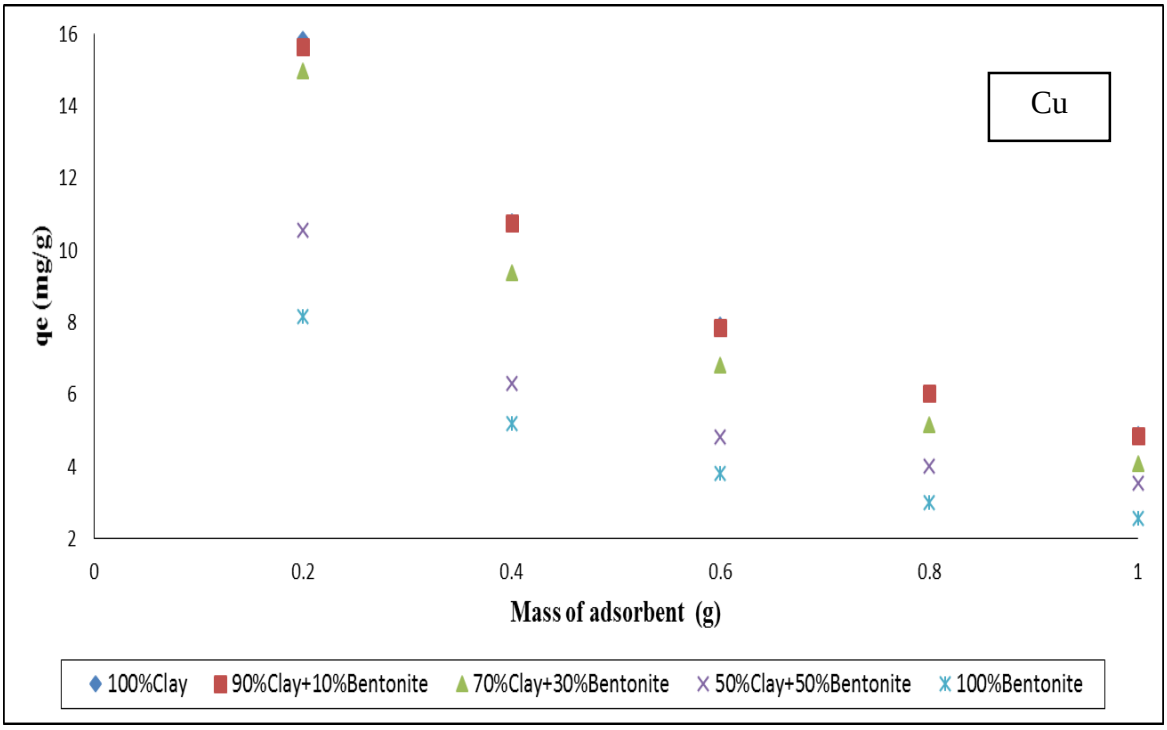


Figure 14: The effect of mass adsorbent on the removal efficiency % of copper and nickel using different mixture ratio of clay and bentonite.

However, at equilibrium the adsorption capacity decreased with increasing in the amount of dosage for all combinations of bentonite and clay as shown in figure 15. Gupta & Bhattacharyya, 2008[34], and Vieira et al., 2010[36] investigated the effect of dosage on metals uptake, and found similar trend. Also, the reported that this trend was presumably due to two reasons: (i) higher adsorbent amount forms particle aggregation, leading to decrease in the total surface area and increase in the diffusion path length both of which lead to decrease in the adsorption capacity, and (ii) as more and more dosage was added results a decrease in the unsaturation of the adsorption sites and therefore, the number of available sites per unit mass reduces resulting in comparatively less adsorption at higher adsorbent amount. Similar findings was investigated by other researchers who studied the effect of dosage on removal of copper and nickel by different types of clays as shown in table 7.

Table 16: The maximum removal efficiency % and adsorption capacity of copper and nickel with different adsorbent mass for all adsorbents at equilibrium time.

Mixture ratio of adsorbent	Adsorbent mass (g)	Copper		Nickel	
		q_e (mg/g)	Removal efficiency %	q_e (mg/g)	Removal efficiency %
100% clay	0.2	15.8	63.38	7.65	30.2
	1	4.88	97.73	2.08	41.7
90% clay + 10% bentonite	0.2	15.6	62.6	8.29	33.2
	1	4.86	97.36	2.4	48.2
70% clay + 30% bentonite	0.2	14.97	59.99	8.63	34.5
	1	4.08	81.7	2.8	55.9
50% clay + 50% bentonite	0.2	10.55	42.2	10.23	40.9
	1	3.5	70.9	2.99	59.98
100% bentonite	0.2	8.16	32.67	8.65	34.62
	1	2.57	51.42	2.67	53.5



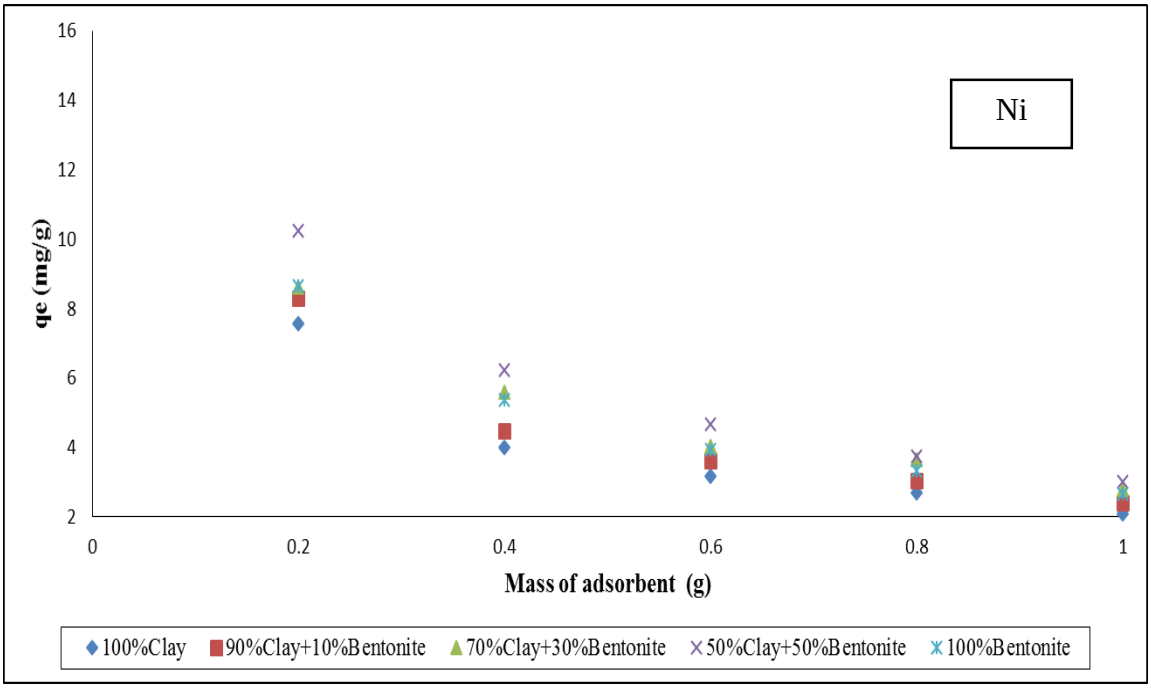


Figure 15: The effect of mass adsorbent on adsorption capacity for copper and nickel onto different mixture ratio of clay and bentonite.

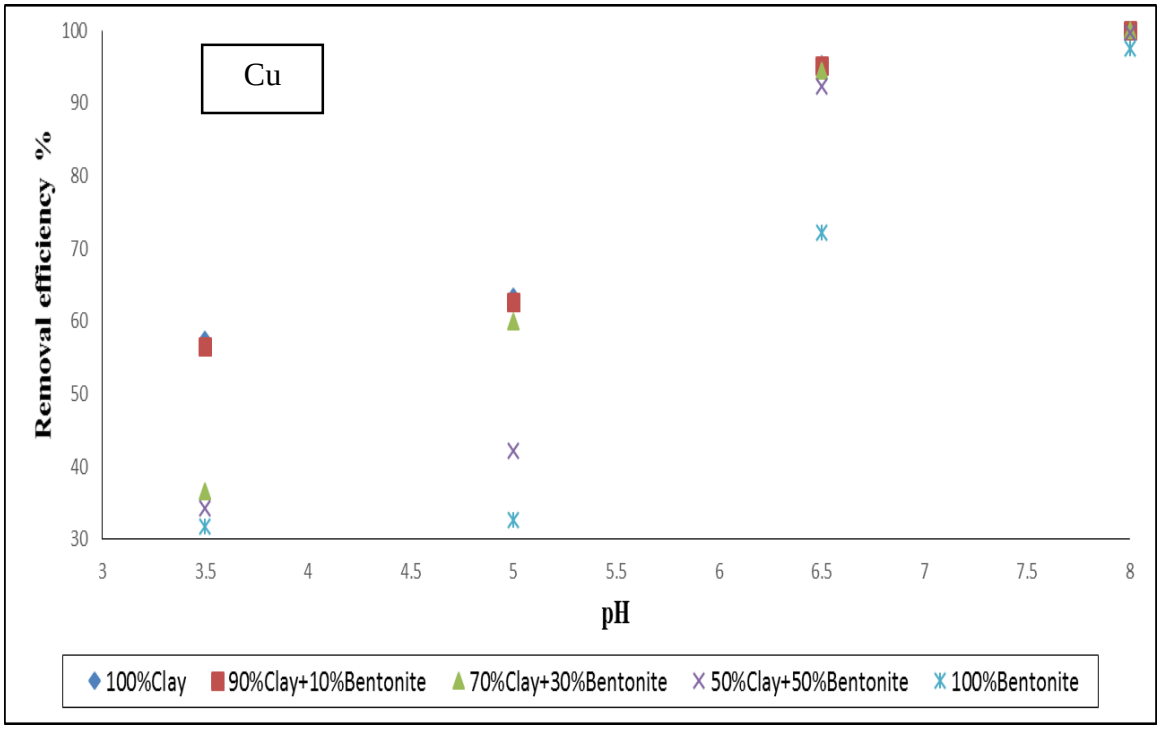
4.2.1.4 Effect of pH

The pH of solution is considered the major factor effecting the adsorption process using clays. Hence, influence of initial solution pH on removal of copper and nickel ions from aqueous solution was studied using bentonite, the combinations of bentonite-clay, and clay alone as adsorbents. This study was carried out under constant conditions of contact time of 240 min and 360 min (at equilibrium) for Cu and Ni respectively at 200 rpm, initial concentration of 100 mg/L, mass of adsorbent of 0.2 g, and temperature of (22±3^{o}C) in the solution pH ranged from 3.5 to 8 (3.5, 5, 6.5and 8).

As presented in figures 16 and 17 for copper and nickel removal, an increase in adsorption capacity and removal efficiency with rising in the initial solution pH from 3.5 to 8. Table 17 shows the maximum removal efficiency and adsorption capacity of copper and nickel with different initial solution pH for all adsorbents at equilibrium time. Ding et al, 2009[12], and Gupta & Bhattacharyya, 2008[35] studied the effect of pH on metals uptake and found similar trend. Also, they reported that this increasing in adsorption capacity and removal efficiency may be attributed to increasing in number of H^{+} ions at low initial pH which compete the metal ions on available adsorption sites while as increase in pH that mean the solution becomes more basic with decreasing in competition between hydrogen ions and metal ions for adsorption sites.

Table 17: The maximum removal efficiency % and adsorption capacity of copper and nickel with different initial solution pH for all adsorbents at equilibrium time.

Mixture ratio of adsorbent	pH of solution	Copper		Nickel	
		q_e (mg/g)	Removal efficiency %	q_e (mg/g)	Removal efficiency %
100% clay	3.5	14.3	57.5	3.6	14.46
	8	24.99	99.96	8.2	32.8
90% clay + 10% bentonite	3.5	14.1	56.6	4.3	17.2
	8	24.99	99.96	8.6	34.67
70% clay + 30% bentonite	3.5	9.15	36.6	6	24.1
	8	24.9	99.9	9.7	39
50% clay + 50% bentonite	3.5	8.57	34.3	7	27.9
	8	24.9	99.9	10.6	42.5
100% bentonite	3.5	7.9	31.7	6.9	27.6
	8	24.38	97	9.48	37.9



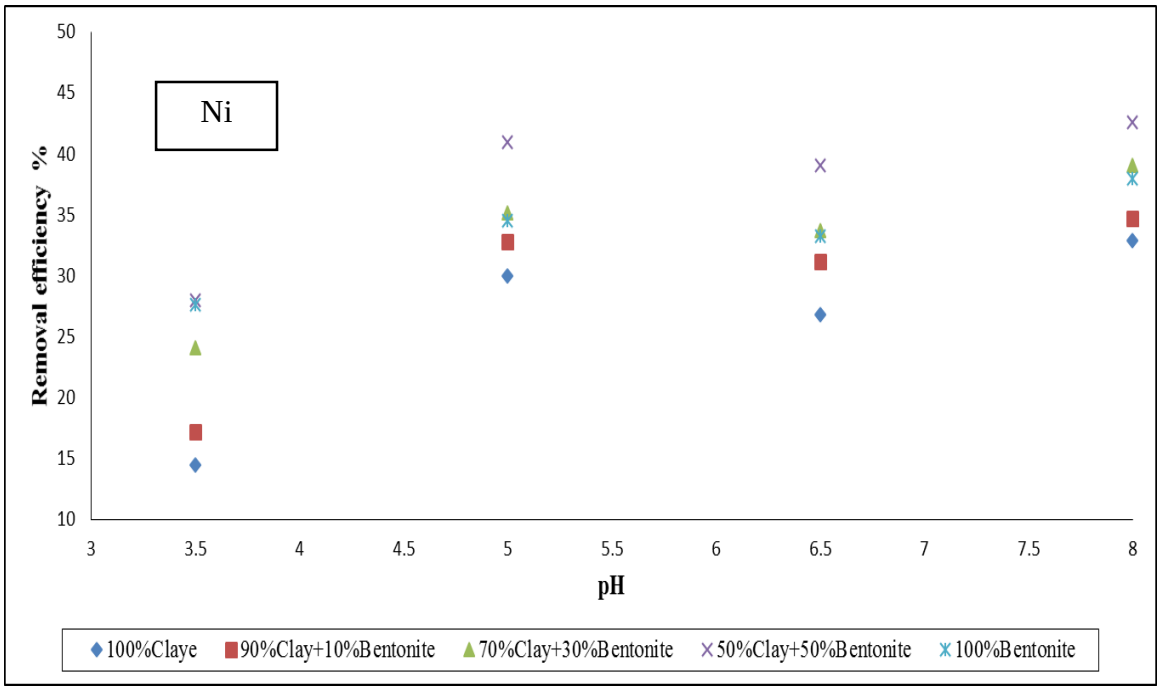
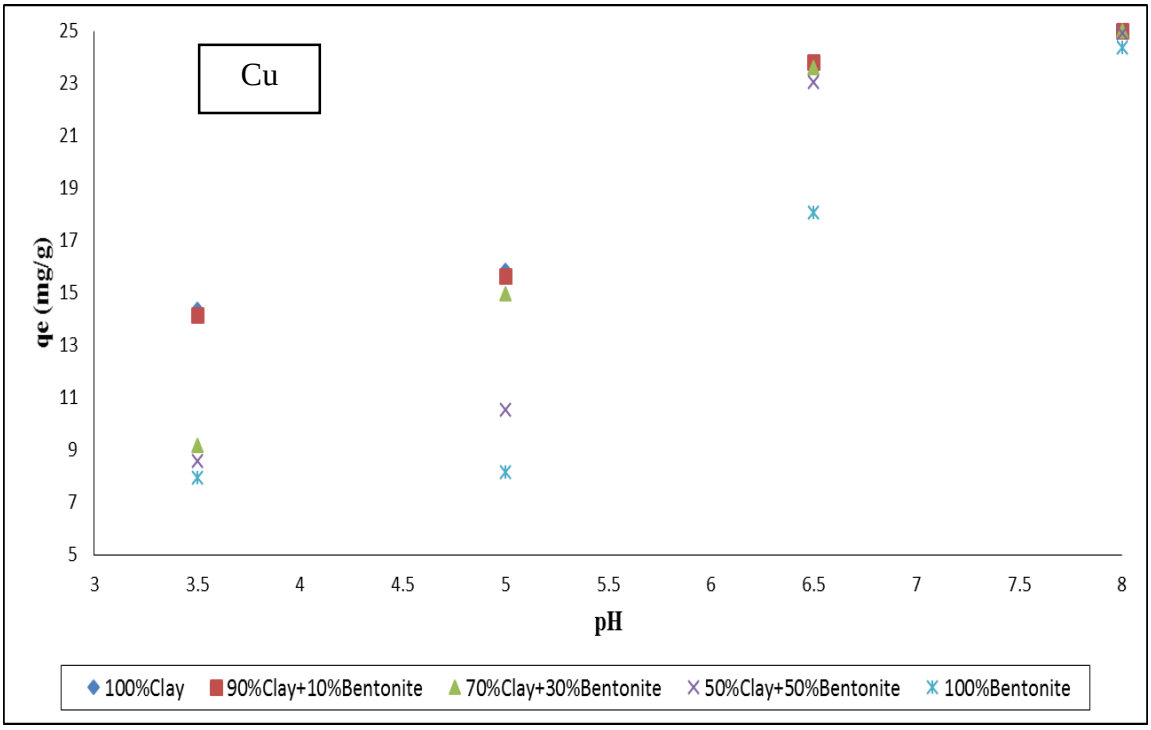


Figure 16: The effect of initial solution pH on the removal efficiency % of copper and nickel using different mixture ratio of clay and bentonite.



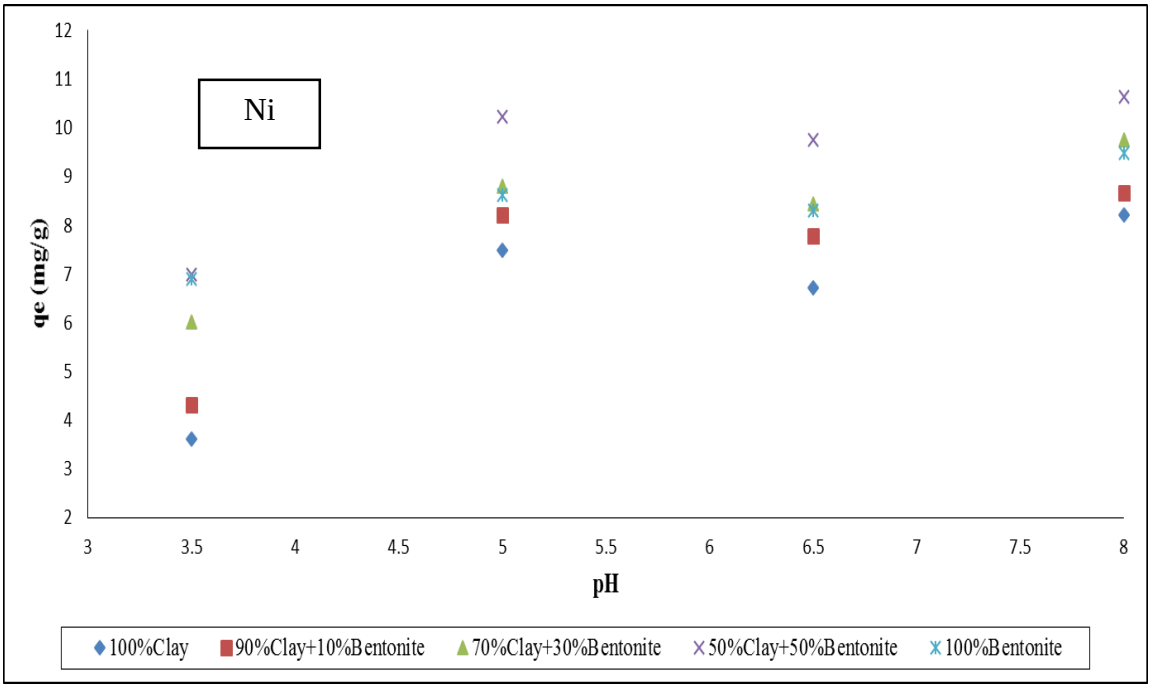


Figure 17: The effect of initial solution pH on adsorption capacity for copper and nickel onto different mixture ratio of clay and bentonite.

However, it cannot carried out the adsorption process at pH more than 6 and 8 for copper and nickel respectively due to precipitation of copper ions as hydroxides as reported by Gupta & Bhattacharyya, 2008[35]. Figure 18 shows the concentration of blank (control) after shaking with different initial solution pH at 100 ppm for copper and nickel at equilibrium time. And it is clearly that there is a removal due to precipitation after pH 6.5 for copper and nickel.

Similar findings has observed by other researchers using different adsorbents. Gupta & Bhattacharyya, 2008[35] studied the effect of pH on removal of copper and nickel and found that increasing in the removal with increasing in the pH of solution. The removal for copper and nickel respectively increased from 4.2 to 17.1% in the pH range 1.0–6 and 11.3 to 60.2% in the pH range 1.0–10 using kaolinite. Also, the removal for copper and nickel respectively increased from 71.7 to 85.7% in the pH range 1.0–6 and 50.1 to 96.4%in the pH range 1.0–10 using montmorillonite.

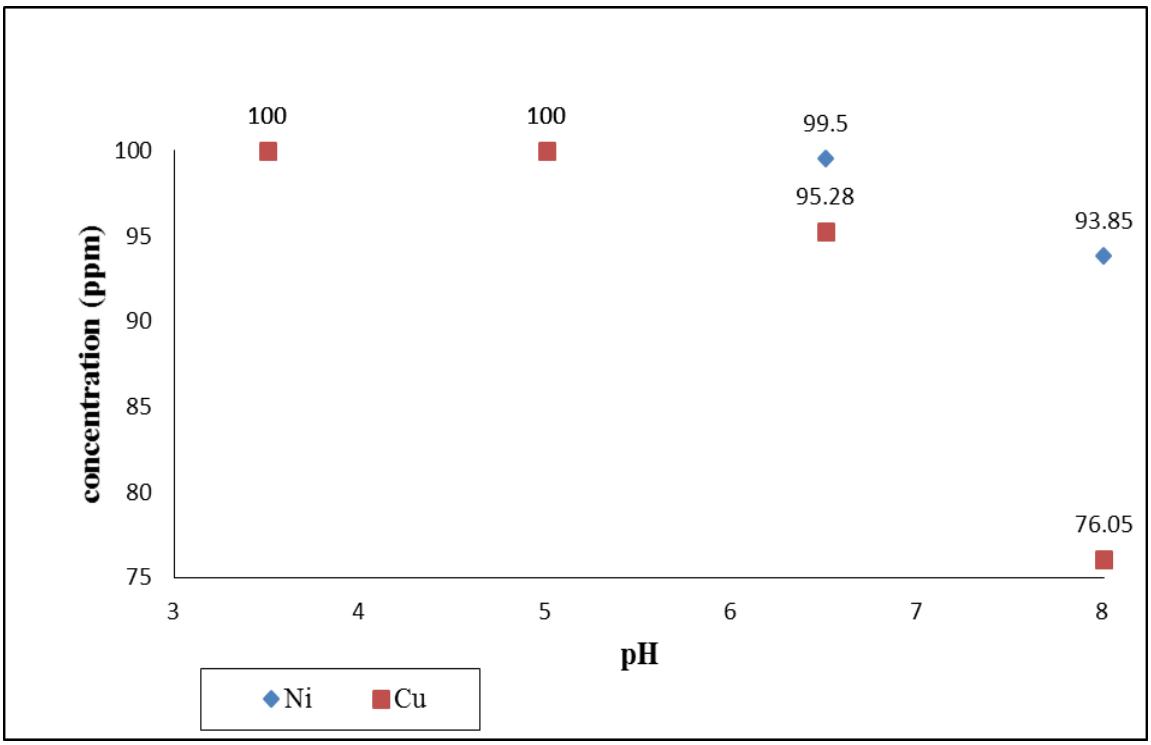
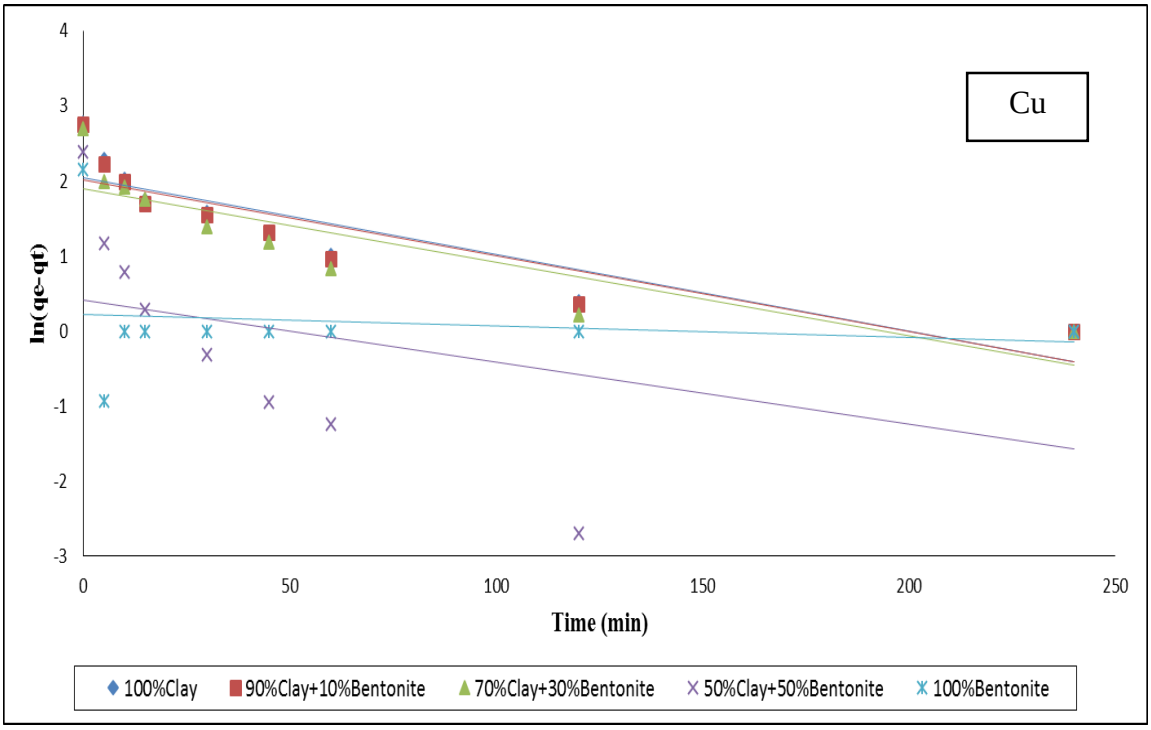


Figure 18: the concentration of blank (control) after shaking with different initial solution pH at 100 ppm for copper and nickel at equilibrium time

4.2.2 Kinetics Study

To identify mechanisms of adsorption process kinetics study was investigated which is fundamental for the successful design in industrial application of adsorption by using same data and conditions observed in the effect of contact time. In order to study the kinetics and these mechanisms of Cu (II) & Ni (II) adsorption on studied adsorbents, the experimental adsorption data was fitted to pseudo-first-order and pseudo-second-order models. Figures 19 and 20 present the pseudo-first-order and pseudo-second-order models respectively.

Moreover, the parameters and expected equilibrium adsorption capacity by model were calculated in table 18. This table also, contains comparing between pseudo-first-order and pseudo-second-order models. From figures 19 and 20 and table 18, it can be seen that the experimental data has a great agreement with pseudo-second-order model for all combination adsorbent of clay and bentonite. The correlation coefficient R^2 ranged from 0.995 to 1 with copper removal and from 0.96 to 0.999 with nickel removal for all combination adsorbent of clay and bentonite.



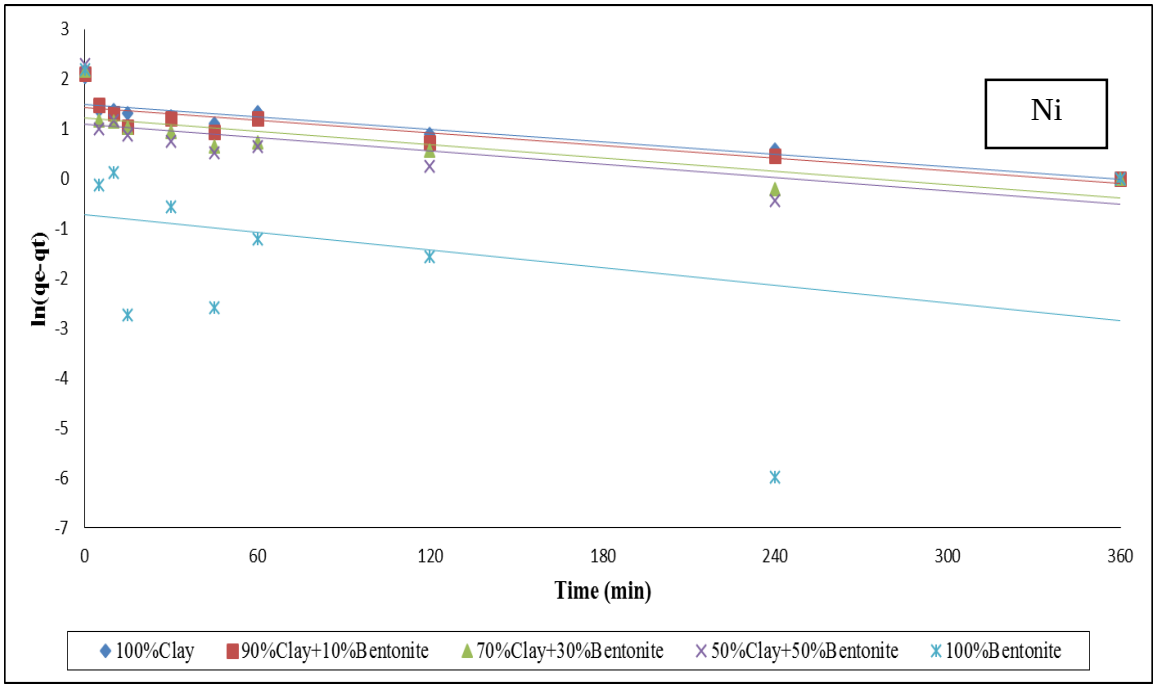
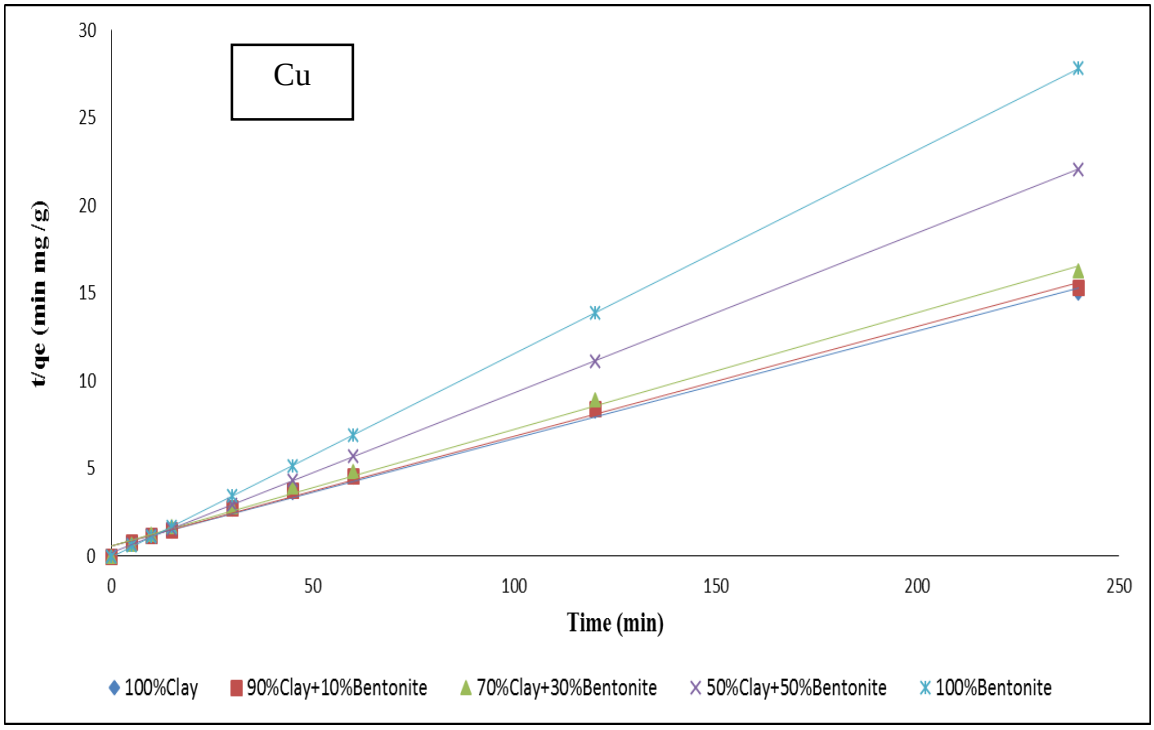


Figure 19: Pseudo-first-order plots for the adsorption of copper and nickel onto clay and bentonite and their combination.

Also, the adsorption capacity q_e value at equilibrium time which obtained from pseudo-second-order model is agreed with the experimental data with small deviation ranged between 0.07 % and 4.47 %. This error may be attributed to the uncertainty in the experimental dat. And the pseudo-first-order model has a small correlation coefficient R^2 especially with 100 bentonite. Furthermore, it is not adequately experimental equilibrium adsorption capacity as a result it was not applicable. This mean that the mechanism of adsorption process may be controlled by chemical adsorption including ion exchange between adsorbent and adsorbate as reported by Ho & McKay[25], and Plazinski et al[27]. The similar trend was observed by other researchers for adsorption of copper and nickel ions onto different clays. Bhattacharyya & Gupta[35], Vieira et al[36], Koyuncu & Kul[43] and Zhi-rong[49] reported that the pseudo-second-order model is more suitable if compared with pseudo-first-order model.



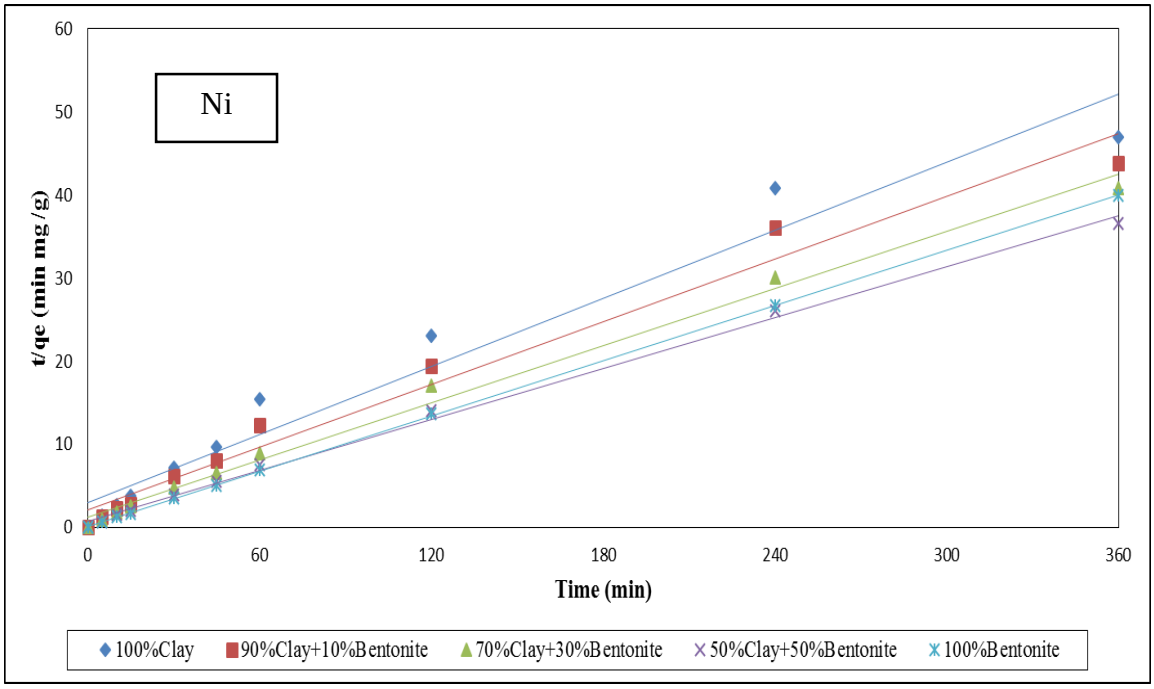


Figure 20: Pseudo-second-order plots for the adsorption of copper and nickel onto clay and bentonite and their combination.

Table 18: Pseudo-first- order and pseudo-second-order parameters for the adsorption of a) Cu b) Ni.

Type of adsorbents	Model	R^2	K	qe (mg/g)	
				Experimental	Expected
100 % Clay	1st	0.796	0.010	16.0125	7.75
	2nd	0.996	0.102		16.34
90% Clay + 10% Bentonite	1st	0.791	0.0101	15.6675	7.51
	2nd	0.996	0.103		15.97
70% Clay + 30% Bentonite	1st	0.758	0.0098	14.7475	6.70
	2nd	0.996	0.112		15.01
50% Clay + 50% Bentonite	1st	0.188	0.0083	10.8675	0.42
	2nd	0.999	0.529		10.95
100% Bentonite	1st	0.0225	0.0016	8.6275	1.25
	2nd	1	-3.558		8.62

a) For Copper

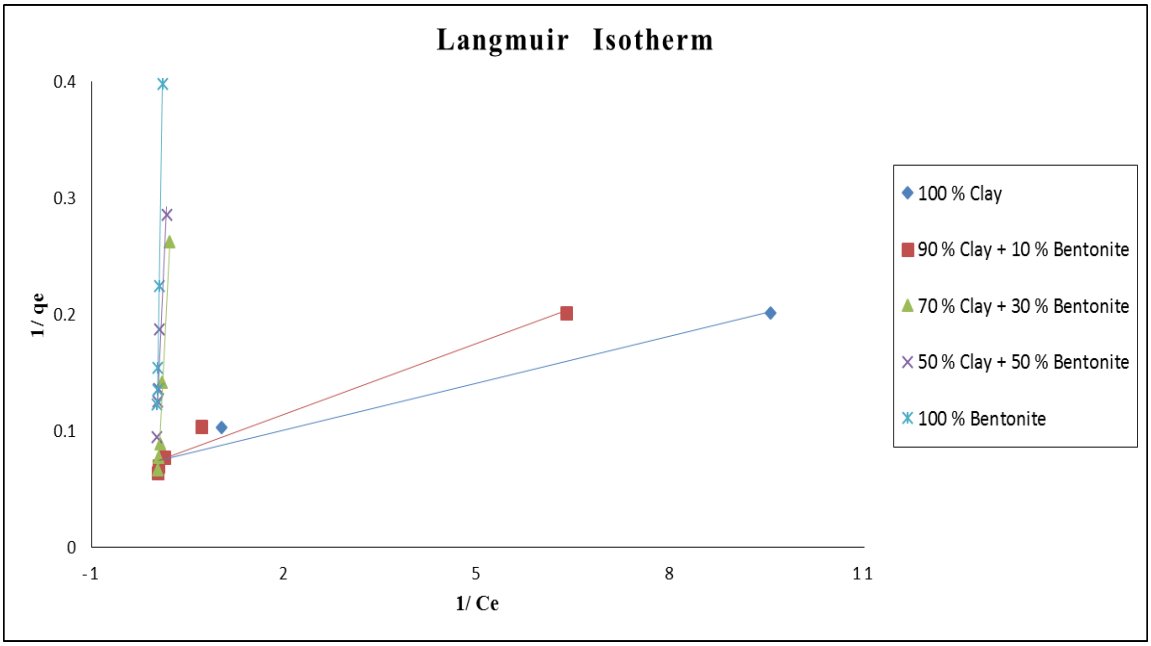
Type of adsorbents	Model	R^2	K	qe (mg/g)	
				Experimental	Expected
100 % Clay	1st	0.851	0.0042	7.67	4.47
	2nd	0.959	0.0452		7.33
90% Clay + 10% Bentonite	1st	0.763	0.0042	8.22	4.13
	2nd	0.977	0.061		7.9
70% Clay + 30% Bentonite	1st	0.640	0.0044	8.81	3.36
	2nd	0.993	0.0992		8.70
50% Clay + 50% Bentonite	1st	0.538	0.0045	9.84	3.03
	2nd	0.997	0.14		9.7
100% Bentonite	1st	0.104	0.006	9	2.05
	2nd	0.999	0.885		9.01

b) For Nickel

4.2.3 Isotherm Study

The adsorption isotherm was investigated for copper and nickel removal to evaluate the applicability of adsorption processes as a unit operation and find the relation between metal concentrations in the liquid phase with metal concentration in solid phase at the equilibrium. In order to study the adsorption isotherm of Cu (II) & Ni (II) on studied adsorbents, the experimental adsorption data that observed under same conditions of effect of initial concentration was fitted to Langmuir and Freundlich models. Figure 21 shows the plots of Langmuir model ($1/q_e\ VS.\ 1/C_e$) and Freundlich model ($Log\ q_e\ VS.\ Log\ C_e$) respectively for removal of copper using the five combination of clay and bentonite.

In this research work, it is clearly that the results of copper and nickel removal have a good fitting with both Langmuir and Freundlich isotherm models for all adsorbent with high correlation coefficients of 0.941 to 0.996 and 0.93 to 0.974 for copper and of 0.957 to 0.997 and 0.914 to 0.997 for nickel respectively for all the adsorbent as can be observed from figure 21 and 22. This can be can be interpreted by that the adsorption sites in nature may be formatted of both of the monolayer and heterolayer as reported by Malamisa & Katsou[28]. Tables 19 and 20 show the constant values for both Langmuir and Freundlich isotherms of copper and nickel removal respectively.



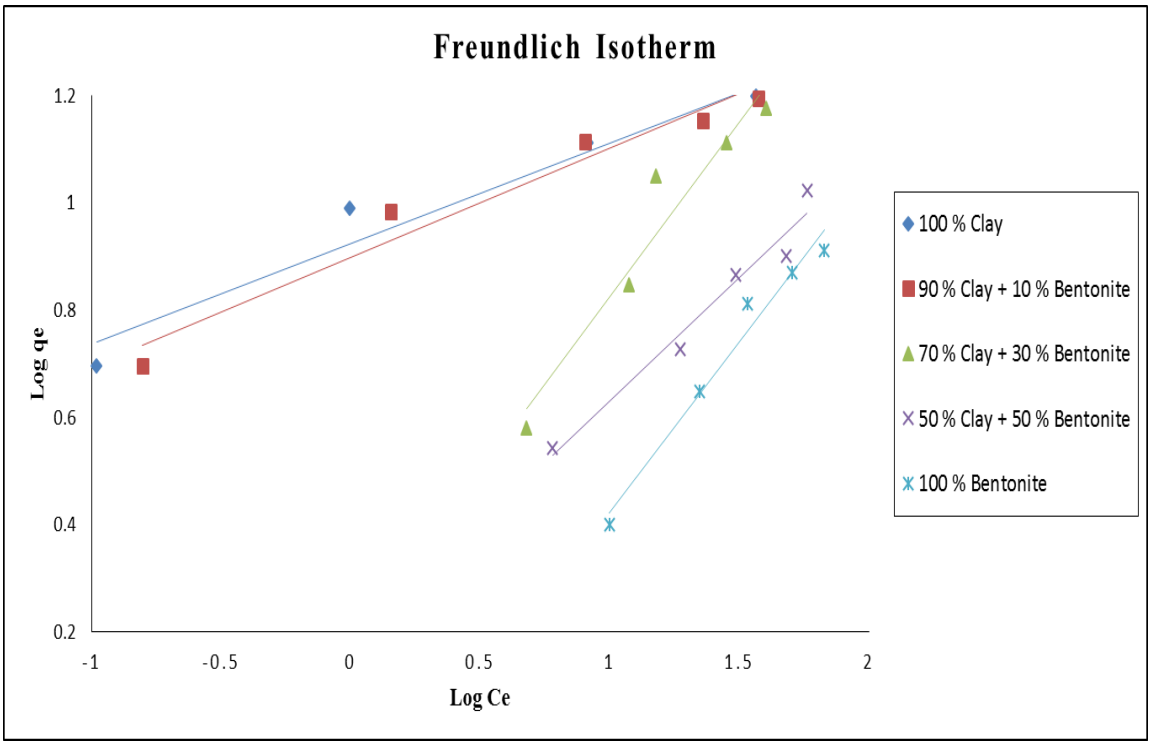


Figure 21: Langmuir and Freundlich isotherm plots for the adsorption of copper onto clay and bentonite and their combination

Table 19: Langmuir and Freundlich isotherm adsorption parameters for removal of Cu.

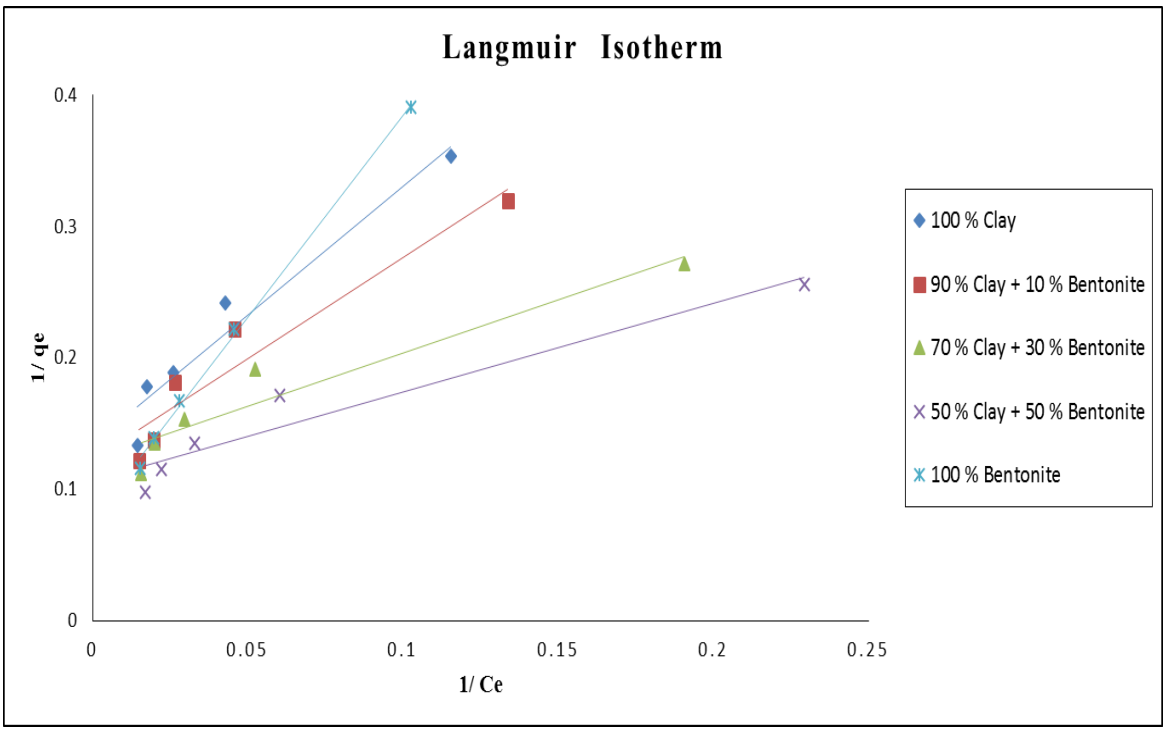
Type of adsorbents	Freundlich Isotherm			Langmuir Isotherm			
	R^2	n_f	k_f	R^2	q_{max}	k_L	R_L
100 % Clay	0.95	5.34	8.38	0.97	13.55	5.466	0.0036
90% Clay + 10% Bentonite	0.96	4.90	7.91	0.97	13.56	3.630	0.0054
70% Clay + 30% Bentonite	0.93	1.53	1.49	0.97	27.24	0.034	0.37
50% Clay + 50% Bentonite	0.96	2.17	1.48	0.94	10.21	0.083	0.193
100% Bentonite	0.97	1.57	1.62	0.99	14.40	0.022	0.4855

Table 20: Langmuir and Freundlich isotherm adsorption parameters for removal of Ni.

Type of adsorbents	Freundlich Isotherm			Langmuir Isotherm			
	R^2	n_f	k_f	R^2	q_{max}	k_L	R_L
100 % Clay	0.95	2.33	1.10	0.94	7.44	0.068	0.225
90% Clay + 10% Bentonite	0.96	2.28	1.23	0.91	8.19	0.079	0.201
70% Clay + 30% Bentonite	0.97	2.96	2.03	0.91	8.14	0.151	0.116
50% Clay + 50% Bentonite	0.98	2.78	2.23	0.93	9.42	0.157	0.113
100% Bentonite	0.99	1.59	0.62	0.99	12.9	0.025	0.442

From tables 19 and 20, it can be observed that the constant coefficients of n_f for Freundlich isotherm ranged from 1.53 to 5.34 for copper and from1.6 to 2.96 for nickel. This indicate that a decreasing in affinities with increasing in adsorption density (i.e. conformity of the data to multilayer formation at the adsorbent surface) because the values of n_f are larger than one [23]. Also, it can be observed that the Freundlich adsorption capacity coefficients k_f has values of 1.48 to 8.38 and of 0.6 to 2.23 for copper and nickel respectively. The Freundlich adsorption capacity coefficients with copper are higher than that with nickel. Also in compering between adsorbents, the highest value is found with clay alone in removal copper and with 50 % clay + 50 % bentonite in removal nickel.

Moreover, the Langmuir equilibrium coefficients k_L has values of 0.022 to 5.466 and of 0.025 to 0.157 for copper and nickel respectively. According to Vieira et al[36] and Gupta & Bhattacharyy[33] this parameter determine the direction of movement the equilibrium interaction; Clay (adsorbent) + Metal (adsorbate) = Clay---Metal. Also they reported that higher value indicate that the equilibrium shifts to the right side, with the resulting formation of the adsorbate–adsorbent complex. It is clearly that the interaction between copper and adsorbents stronger than nickel and adsorbents. Also in removal copper, higher value of 5.466 for clay alone indicate that the interactions strongest between copper and clay. While in removal nickel, the strongest interactions between nickel and 50 % clay + 50 % bentonite is with largest values of 0.157.



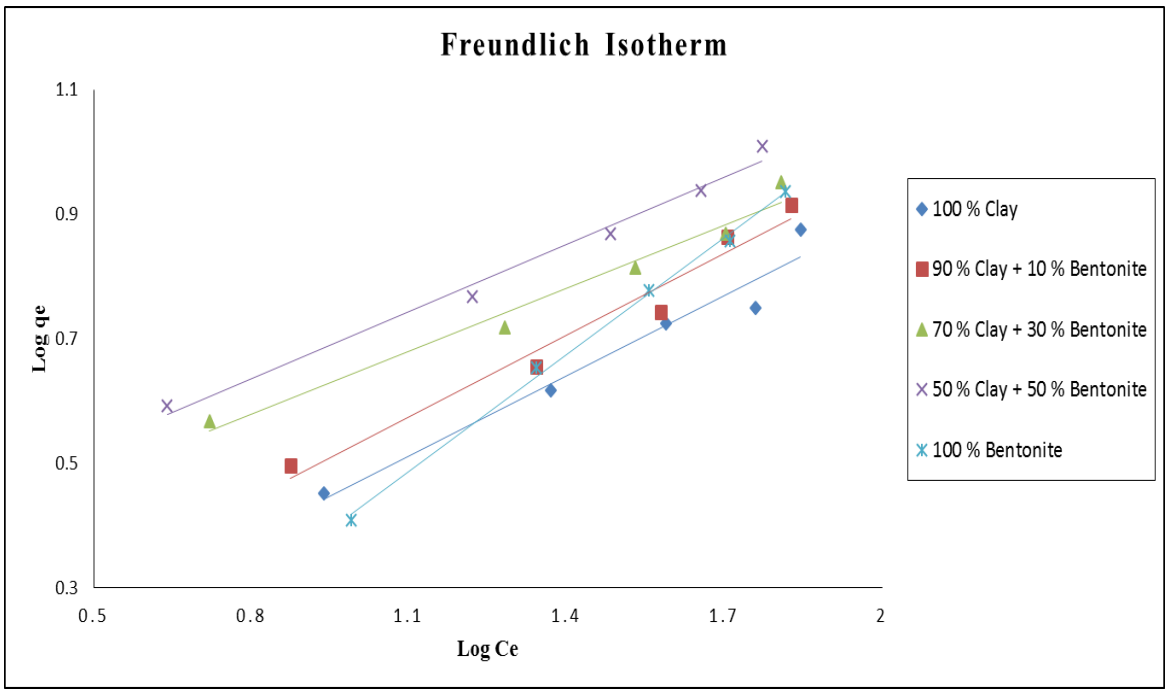


Figure 22: Langmuir and Freundlich isotherm plots for the adsorption of nickel onto clay and bentonite and their combination.

Furthermore, the constant coefficients of R_L for Langmuir isotherm ranged from 0.0036 to 0.485 and from 0.113 to 0.442 for copper and nickel respectively. This mean that the adsorption of copper and nickel ions are favorable because the separation factors R_L are ranged between 0 and 1[36]. Many researchers studied the isotherm for adsorption of copper and nickel and they found similar trend is discussed in chapter 2 and presented in table 3.

[CHAPTER 5]

CONCLUSIONS AND RECOMMENDATIONS

5.1 Summary

This work investigated that the removal of copper and nickel from wastewater using Saudi Arabian bentonite, clay and different ratios of combinations of bentonite-clay. The clay material and bentonite were obtained from various sites in the Eastern Province of Saudi Arabia and were thoroughly characterized using SEM, BET, CEC, XRF and XRD techniques. The parameters which were investigated are the effect of shaking time with effect of ratio of bentonite to clay. Also, effect of changing in pH of solution as well as the mass of dosage and varying in initial concentration were investigated. The results show that the ratios of bentonite to clay have an important impact on the adsorption capacity of copper and nickel. In addition, the adsorption capacity (q_e) of copper and nickel was very fast in the first few minutes and then decreased until the equilibrium had been reached. The equilibrium was established at 30 min with q_e of 8.7 mg/g for copper and 45 min with q_e of 8.9 mg/g for nickel with 100 % bentonite, and 240 min with q_e of 16 mg/g for copper and 360 min with q_e of 7.7 mg/g for nickel with 100% clay.

Finally, the clay, the combinations of bentonite-clay, and bentonite alone demonstrated efficient removal of copper and nickel as a result these mixtures can considered to as a good alternative to the widely used activated carbon in the treatment of the wastewater containing metal ions by adsorption.

5.2 Conclusions

Based on the outcome of this research, it is concluded that:

1. Saudi Arabian clay and bentonite tested can be considered as an excellent adsorbent for the removal of copper and nickel from wastewater.
2. The chemical and physical properties of both metals as well as adsorbent have significant impact on removal efficiency.
3. The ratios of bentonite to clay have significant impact on the adsorption capacities of copper and nickel where an increase in this ratio results in a decrease in the adsorption capacity of copper. Conversely, an increase in this ratio results in an increase in the adsorption capacity of nickel.
4. The initial contact time has significant impact on the adsorption capacities (q_e) of copper and nickel where the removal was very fast in the first few minutes and then decreases until the equilibrium is reached.
5. The equilibrium was reached with bentonite faster than with clay. The equilibrium was established at 30 min and 45 min with bentonite alone, and 240 min and 360 min with clay alone for copper and nickel respectively.

6. The adsorption capacity and removal efficiency also affected by the amount of adsorbent added to the solution. As the amount of adsorbent increases, the removal efficiency increases while the adsorption capacity decreases for all combination of the adsorbents.
7. The pH plays important role in removal copper and nickel, as increasing in pH of solution, the adsorption capacity as well as the removal efficiency also increases. The removal increases from 57 to 95 % and 14 to 27 for Cu and Ni respectively with an increase in pH from 3.5 to 6.5 using clay alone as adsorbent. The removal increases from 31 to 72 % and 27 to 33 for Cu and Ni respectively with an increase in pH from 3.5 to 6.5 using bentonite alone as adsorbent.
8. The initial metal ion concentration affects the adsorption capacity and removal efficiency. The removal efficiency decreases while the adsorption capacity increases with an increasing in the initial metal ion concentration of Cu and Ni for all combination of the adsorbents.
9. The pseudo-second-order model describes the mechanism of removal of copper and nickel for all combination of clay and bentonite.
10. Furthermore, Langmuir and Freundlich models describe the isotherm of removal of copper and nickel for all combination of clay and bentonite.

5.3 Future Research

Based on the results and findings of this research, following suggested points can be considered in further:

1. The effect of other factors not considered in this work such as temperature of solution and shaking speed should be investigated.
2. Study the competitive adsorption between copper and nickel ions.
3. Study the adsorption onto clay and bentonite with other metal ions like lead, cadmium, and cobalt.
4. Investigate the effect of chemical/physical modification of clay and bentonite to improve their adsorption properties.

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